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I am submitting herewith a dissertation written by Robert Allen Bowling entitled "High-Temperature Photoelectron Spectroscopy of Alkali Nitrate, Metaphosphate, and Cyanide Vapors." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

George K. Schweitzer, Major Professor

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HIGH-TEMPERATURE PHOTOELECTRON SPECTROSCOPY OF ALKALI NITRATE, METAPHOSPHATE, AND CYANIDE VAPORS

A Dissertation

Presented for the

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Degree

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ABSTRACT

The high-temperature He(I) photoelectron spectra of the gas-phase molecules KNO_3, $RbNO_3$, $CsNO_3$, $NaPO_3$, KPO_3, $RbPO_3$, $CsPO_3$, NaCN, and KCN have been obtained. The vapors were produced by resistance heating a tantalum-strip-wound quartz sample oven which was coated with a high-temperature ceramic cement. Analysis of the ejected electrons was carried out using a modified truncated cylindrical-mirror electron spectrometer. Assurances regarding the identities of the vapor-phase species were had by using data obtained from the techniques of electron diffraction, mass spectrometry, microwave spectroscopy, and matrix-isolation and vapor infrared spectroscopies. The ionization energies were assigned molecular orbital origins through the use of molecular orbital calculations, comparisons with X-ray, He(I), and He(II) photoelectron data for the solids, and analogies with other compounds of similar type.

Observations concerning the similarities of the spectra of all compounds containing the same anion and concerning the correlation of the experimental data with theoretical calculations for the corresponding free anions led to the possibility that a high-temperature structural model called polytopic bonding might be applicable to these vapor species. The observed spectral band breadths, however, were considerably greater than the splits expected on the basis of theoretical calculations for various structural parameter changes. It was, therefore, concluded that no judgment could be made concerning the possible polytopicity of these compounds at high temperatures.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

A. Experimental Investigation of Molecular Orbitals

In recent times the experimental investigation of molecular orbital (MO) configurations and ionization energies has yielded important information for use by chemists and chemical physicists in the understanding of molecular bonding. The value of obtaining such electronic information cannot be overestimated since many properties of molecules can be related to their MO formalisms. Until the past decade the principal methods of experimentally determining atomic and molecular orbital ionization energies were classical optical spectroscopy, X-ray absorption spectroscopy, X-ray emission spectroscopy, and mass spectrometry. The single-electron ionization energies obtained by these methods have been related through various considerations to theoretical binding energies of the electrons in the atomic or molecular sublevels or orbitals of the un-ionized atom or molecule.

Carefully measured positive ion appearance potentials obtained from mass spectrometric investigations of vapor atoms and molecules can in some instances provide good approximations of the outermost orbital ionization energies of these species. Experimentally the vapor molecule or atom is bombarded by an electron beam or photon source in a sample ionization chamber. The energy of the ionization source is gradually increased from zero until positive ions are detected. An appearance potential curve is usually constructed by plotting the positive

ion intensity against ionization source energy. The source energy at which ion formation first occurs is taken to be the appearance potential of the most readily formed ion and also as the first ionization energy of the atom or molecule. Usual errors are on the order of 0.1 to 0.3 eV. Accurate appearance potentials are difficult to obtain and can only give values for first ionization energies. Nevertheless, the values obtained from cautious studies may often be usable as approximations within a few percent.[1]

Classical optical spectroscopic techniques (both emission and absorption) are generally applicable to outer electrons and have been principally applied to atomic species, primarily because the energetics of molecular vaporization are often high enough to dissociate some or all bonds. Substances are vaporized principally by flames, furnaces, arcs, sparks, and discharges to produce free atomic species. With the input of excess energy from the vaporization source, outer electrons may be excited to higher energy levels. When the atoms de-excite, the electrons may drop to lower energy levels and emit radiation, measurement of which permits determination of the energy difference between involved levels. In addition extrapolation of Rydberg series of transitions to obtain values for the removal of an electron from a level to the continuum has proven to be a good method of estimating orbital ionization energies. Alternately, if continuous source radiation is passed through the volatilized atoms, they may absorb specific wavelengths thus exciting an electron to a higher energy level. Measurement of the absorbed wavelengths permits determination of the energy difference

between involved levels. Rydberg series extrapolation again may permit determination of absolute ionization energies.[2]

X-Rays may be absorbed by atoms or molecules in a process involving the transfer of the photon's total energy to an electron which is then ejected, the process occurring with enhanced intensity when the X-ray energy just equals the energy needed to remove the electron. When a substance is irradiated with a spectral array of X-rays, the energies which correspond to removal of certain electrons (called absorption edges) may often be obtained. Most experiments have been carried out on solid elements and compounds with only a few investigations having been made on gaseous species. Therefore, corrections must generally be applied to the solid data to obtain estimates for the free atoms or molecules. (These corrections usually involve the work function of the solid, adjustment to zero charge in the case of atomic species, and adjustments for matrix influences in the case of molecules.)[3]

If an atom or molecule is bombarded with ions, electrons, or photons with enough energy to eject an inner electron, the hole may be filled by the drop-in of an outer orbital electron with an X-ray having an energy approximately equal to the orbital energy difference being emitted. Many studies have been carried out on solid species, and a significant number of studies have been carried out on gaseous species. In the case of solids, corrections as discussed for X-ray absorption must be applied to obtain values for free atoms or molecules. In the case of gaseous molecular species, corrections must be applied to obtain values for free atoms. Some transition selection rules are also applicable to X-ray emission. These limit the amount of data obtainable

because some transitions are not allowed. The major selection rules are: (1) the triple product of the group symmetrics of the initial state, the electric dipole transition operator, and the final state must contain the totally symmetric irreducible representation for the transition to be allowed; (2) transitions are allowed only from orbitals of an atom to other orbitals of the same atom; and (3) there must be a change in the atomic quantum number ℓ of ± 1 for the transition to be allowed.[4]

As can be seen by these brief treatments, the atomic and molecular orbital data obtainable by these methods are somewhat limited especially for molecular species and especially for free atoms and molecules in the vapor state. With the development of more intense monoenergetic photon sources in recent years the technique of photoelectron spectroscopy (PES) has emerged as a very good and much preferred method for determining atomic and molecular orbital ionization energies, the principal reasons being that well resolved absolute ionization energies are obtainable rather than differences between levels, and no levels are inaccessible due to functioning of selection rules. The method will be described in more detail in the next sections.

B. Photoelectron Spectroscopy

The history of photoelectron spectroscopy extends back to the explanation of the photoelectric effect by Einstein in 1905.[5] The full potential for the use of photoelectron spectroscopy as a chemical problem-solving technique was not realized until the development of electron spectrometers of high resolving powers. This did not come until early

in the last decade. The history of photoelectron spectroscopy is well described and voluminously detailed in many good books and review articles on the subject and will not be described here.[6]

The photoelectric effect is a dipole interaction in which the energy of an incident photon is completely expended in the ejection of a bound electron. In competition with this process, photons may also undergo inelastic scattering processes (Compton effect) but this effect is negligible for photon energies of less than about 5 keV. In a typical photoelectron experiment a substance is irradiated with a beam of monoenergetic photons of known energy. (The principally used photon sources are the He(I) (21.22 ± 0.005 eV) and He(II) (40.81 ± 0.005 eV) ultraviolet discharge sources and the $A\ell K_\alpha$ (1486.6 ± 0.5 eV) and MgK_α (1253.6 ± 0.4 eV) X-ray sources.) The electrons ejected in the photoelectric process are then subjected to energy analysis in an electron spectrometer, either an electrostatic or magnetic type. Results are usually obtained as a plot of electron intensity against electron kinetic energy. The electron ionization energies may be approximated by subtraction of the electron kinetic energies from the energy of the impinging photons. This is a good approximation although factors such as the recoil energy of the resultant ion and the work function of the spectrometer surfaces must be considered. Fortunately the recoil energy is negligible for all but the very smallest species and the work function of the spectrometer should remain constant so that the introduction of a calibrant can correct for this latter difference. These electron ionization energies may usually be related to corresponding theoretical molecular orbital binding energies by certain approximations, the most

important of which is Koopmans' theorem,[7] a "frozen orbital" approximation. It should be made very clear at this point that the electron ionization energies experimentally determined by photoelectron spectroscopic measurements are not equivalent to theoretically-calculated neutral molecule molecular orbital energies. Photoelectron spectroscopic ionization energies are correctly described as the difference between the total energies of a singly charged ion and of the ground state of the neutral molecular precursor. Koopmans' theorem assumes that in the photoelectric process reorganization and/or relaxation of the electrons of the ionized species does not occur. In actuality, relaxation and/or reorganization does occur. In some cases, these effects are nearly constant in the ionization of valence electrons or nearly proportional to their theoretical molecular orbital energies. Therefore, in many cases, good qualitative ordering of MO levels may be possible. In other instances, such as in d-orbital considerations, good correlation is sometimes not possible. Koopmans' theorem, therefore, is only a fair approximation of quantitative binding energy values as theoretically calculated for the un-ionized atom or molecule. Errors of the order of a few percent often occur for inner orbitals and of greater than ten percent for outer orbitals.[8]

In the years since its resurgence early in the last decade, photoelectron spectroscopy has been applied to some atomic and a wide variety of molecular species in both solid and gaseous states. Until recently most work was concentrated in obtaining spectra of gaseous and solid covalent compounds and solid ionic compounds at room temperature. These latter works on ionic compounds have included several studies of species

such as MCN and MNO_3 (where M = alkali metal) which contain complex anions. For the correct correlation of experimental solid PES data with theoretical calculations, the solid PES data should be compared with complicated theoretical treatments which include considerations of all lattice effects. Monomer calculations are in comparison much less complex and less time consuming. Thus, in practice, it has been much simpler to compare these solid state data to theoretical calculations on the free molecular monomer to which corrections for solid state effects have been empirically or semi-empirically added. A seemingly better way to obtain usable molecular orbital ionization data on these ionic complex-anion-containing compounds would be to conduct the PES investigations on the vapor monomers themselves. These vapor PES data could then be related more directly to the theoretical monomer calculations. Solid state corrections would no longer be necessary. The primary problem of concern is that many of these ionic molecules might not volatilize to stable monomer vapor species of the same molecular formula as the original solid state molecule. Fortunately, it has been found that a surprisingly large number of these monomers are stable in the vapor state at high temperatures.

C. High-Temperature Vapors

The technique of mass spectrometry has become the most useful method for measurement of high-temperature vapor compositions. Classical vapor techniques, including static and flow methods, vapor density studies, effusion investigations, and others, have also been applied but most of these are rather ineffective in yielding definitive

information concerning vapor species identifications. The mass spectrometric approach is quite sensitive and wide temperature ranges may be employed. However, ambiguities can be encountered in the interpretation of the neutral molecule origins of certain ions, but these are often resolvable through careful experimentation. Many of the compounds found to be stable in the vapor phase have also been studied by electron diffraction, microwave spectroscopy, and infrared and Raman spectroscopies. These investigations often add confirmation to the mass spectrometric results. Some of the complex-anion compounds which have been found to volatilize to stable vapor species without appreciable decomposition are MOH, MCN, MBO_2, MNO_3, MPO_3, $MReO_4$, M_2SO_4, $MA\ell F_4$, $MA\ell C\ell_4$, $MGaF_4$, and $MInC\ell_4$ (M = Li, Na, K, Rb, Cs, and/or Tℓ). In many cases the corresponding monomer species has been found to be predominant in the vapor. In others the dimer is predominant with significant amounts of monomer, and in some cases other polymers are present. High-temperature photoelectron spectroscopy has been applied to a few of these compounds. This will be discussed in the next section.

D. High-Temperature Photoelectron Spectroscopy

To carry out high-temperature photoelectron spectroscopic studies of inorganic vapors, it is necessary to equip the sample exposure chamber with a device which can be heated to temperatures necessary for the volatilizations. Heating techniques which have been employed include wire-wound resistance heating, laser-beam irradiation, and electron bombardment. Special difficulties are often involved in these high-temperature investigations, the major difficulties being:

(1) interference with energy analysis by magnetic and electric fields arising from the heating device; (2) target molecule deposition on cooler spectrometer surfaces giving rise to local and uneven surface charging which tends to broaden and shift spectral bands; (3) sample reactions with the oven or spectrometer materials; (4) desorption of extraneous substances from spectrometer materials; (5) nonequilibrium volatilization in which nonreproducible mixtures of species occur; (6) uneven volatilization which results in pressure fluctuations producing band-intensity and band-position changes; and (7) vibrational hot banding of the sample molecules. Various modifications in instrumentation, oven design, and sample handling have been made to eliminate or ameliorate most of these problems, and in general reasonable success has been had.

The first high-temperature PES study of the modern era was the He(I) investigation of mercury vapor in 1967 by Frost et al.[9] In 1968, Berkowitz and Walter[10] reported high-temperature studies on thallium(I) chloride, bromide, and iodide. From then the field expanded quite rapidly. The first investigations of simple ionic compound vapors were reported in 1973 by Allen et al.[11] for KCℓ, KBr and KI and by Berkowitz et al.[12] for CsCℓ, CsBr, and CsI. Several other studies by these and other groups on many of the alkali halide vapors were later reported along with quite a few thallium(I) halide and alkaline earth halide vapor studies. The initial application of high-temperature vapor PES techniques to complex-anion-containing compounds was made by Schweitzer et al.[13] for $T\ell NO_3$, $T\ell BO_2$, $T\ell ReO_4$, and $T\ell_2SO_4$, and by Vick et al.[14] for $NaReO_4$, $KReO_4$, $RbReO_4$, and $CsReO_4$. The present study constitutes a

continuation of these efforts to obtain molecular orbital data for complex-anion-containing compounds. The purpose of this study will be described in more detail in the following section.

E. Proposed Problem

In recent years there has been an increasing interest in obtaining ultraviolet photoelectron spectroscopic data on vapors of substances which are solids at room temperature. This interest has stemmed from an attempt to understand better the structure and bonding of high-temperature gas-phase molecules. As yet, very few complex-anion-containing compounds have been investigated, although considerable data have been collected on the gaseous forms of these compounds by mass spectrometry, electron diffraction, microwave spectroscopy, vapor infrared and Raman spectroscopies, and matrix-isolated infrared spectroscopy. In addition, a substantial quantity of X-ray photoelectron data, He(I) and He(II) photoelectron data, and X-ray emission data for the solid compounds is available along with numerous theoretical MO calculations for the free anions and compounds. The present study is an effort to continue the investigation of complex-anion-containing compounds at high temperatures in an attempt to gain information on the gaseous forms of these species for comparison with results from mass spectrometry and other experimental techniques and for comparison with theoretical MO calculations. It is hoped that these investigations can provide some definitive information on the structural and bonding characteristics of these vapors and possibly provide insight into future applications of high-temperature PES to chemical problems.

The instrumental, sample handling, and spectral accumulation techniques used in the present studies are the same as for several previous investigations. These have been described in detail already and will not be discussed here.[11,13,14] Any special sample handling procedures will be discussed in the respective experimental sections.

Specifically, since several mass spectrometric studies have shown that the vapors over the heated alkali nitrates, metaphosphates, and cyanides are composed of the corresponding stable monomers and in some cases varying amounts of dimers and other polymers, the purpose of this study was to obtain the high-temperature PES spectra of as many of these monomer species as possible. Once obtained it was aspired that these data could be correlated with the theoretical monomer calculations in hope of obtaining a better understanding of the high-temperature bonding characteristics of these molecules.

CHAPTER II

THE ALKALI NITRATES

A. Abstract

The He(I) photoelectron spectra of the high-temperature gas-phase molecules KNO_3, $RbNO_3$, and $CsNO_3$ have been obtained using a modified cylindrical-mirror electron spectrometer equipped with an internally-located, resistance-heated sample oven. Attempts to obtain data for $LiNO_3$ and $NaNO_3$ were unsuccessful because of decomposition. The identities of the vapor-phase molecules were determined by using data derived from the techniques of electron diffraction, mass spectrometry, and matrix-isolated infrared spectroscopy. The ionization energies were assigned molecular-orbital origins through the use of MO calculations, comparisons with X-ray and He(II) photoelectron data from investigations of solids, and analogies with other compounds of similar type.

B. Introduction

The results of several studies of the vapors over heated alkali metal nitrates indicate differing degrees of stability for $LiNO_3$, $NaNO_3$, and KNO_3 depending on the pressure, the atmosphere, the composition of the sample container, the rate of heating, and the presence of impurities, especially water. The data from mass spectrometric investigations on $LiNO_3$ and $NaNO_3$ may be taken to indicate considerable decomposition in the 650-750°K range; however, similar studies of $RbNO_3$ and $CsNO_3$ indicate little or no decomposition in the vapor state. These studies

and others of related interest which attribute stability to at least some of the alkali-metal nitrates prompted this ultraviolet photoelectron spectroscopic investigation of the vapors over heated $LiNO_3$, $NaNO_3$, KNO_3, $RbNO_3$, and $CsNO_3$.

C. Experimental Procedure

Lithium nitrate, sodium nitrate, and potassium nitrate were obtained from the J. T. Baker Chemical Company and rubidium nitrate and cesium nitrate were obtained from Research Organic/Inorganic Chemical Corporation. All were quoted as being at least 99.9 percent pure and, except for drying, were used as obtained.

All spectral measurements were made employing a truncated cylindrical-mirror analyzer (as previously described[11]) equipped with a resistance-heated tantalum-strip-wound quartz cell coated with Astroceram, a high-temperature ceramic cement obtained from Chemo-Thermic Industries. The cell was heated by a 0-12 volt AC pulse supply. The procedures for sample heating and spectral accumulation have been described previously[13] and will not be repeated here.

D. Results

Representative spectra of the vapors above heated KNO_3, $RbNO_3$, and $CsNO_3$ are presented as Figures 1-3 (pp 14-16). Each is typical of 25 or more spectra obtained for each compound. The unlabeled peak in each spectrum is due to a methylene chloride band (either the one at 11.52 eV or the one at 12.22 eV) which was employed as a calibrant.[15] The values assigned to the peaks for each compound are listed in Table I (p 17). The values represent unweighted averages of the values taken

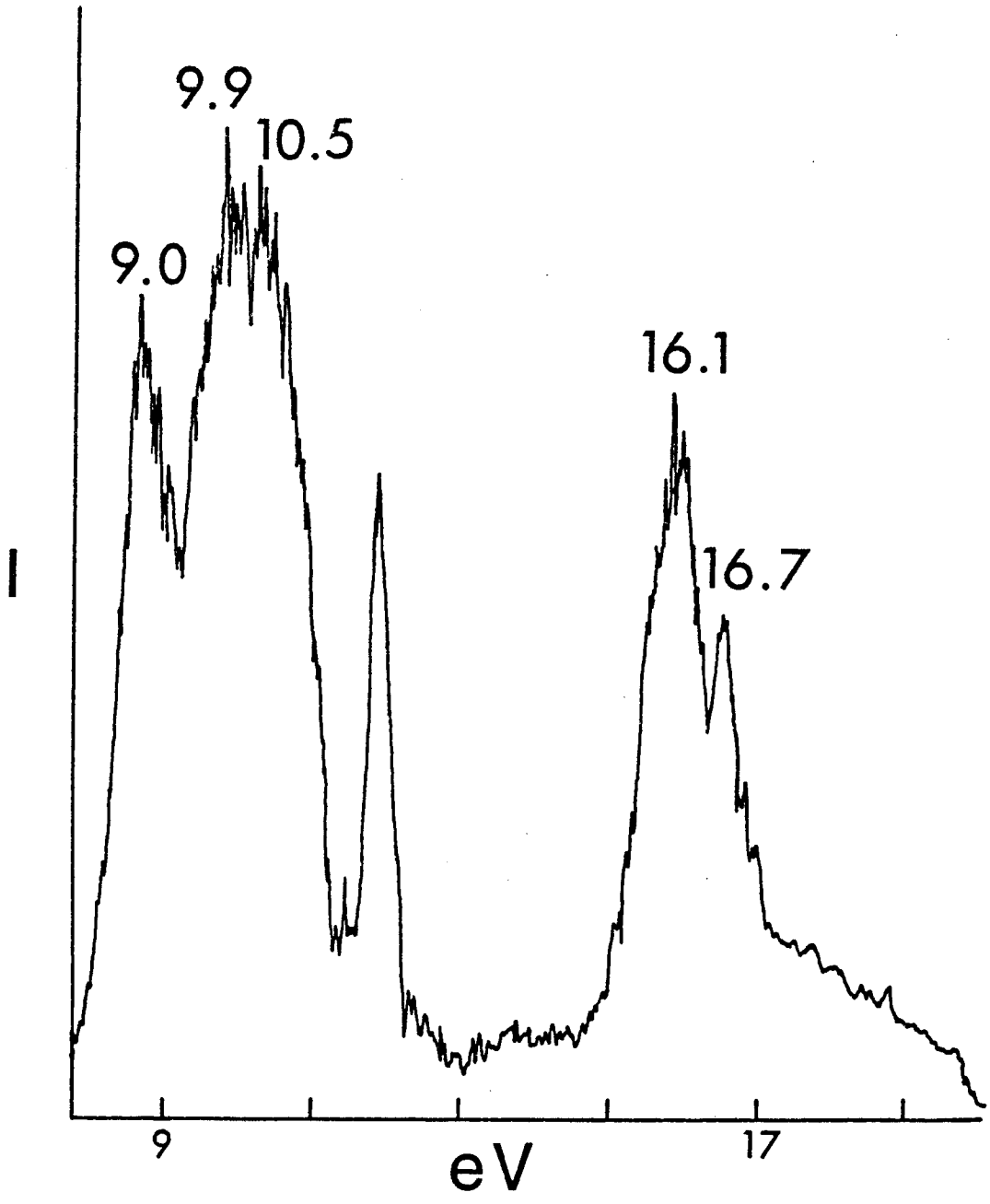

Figure 1. He(I) photoelectron spectrum of KNO_3 vapor.

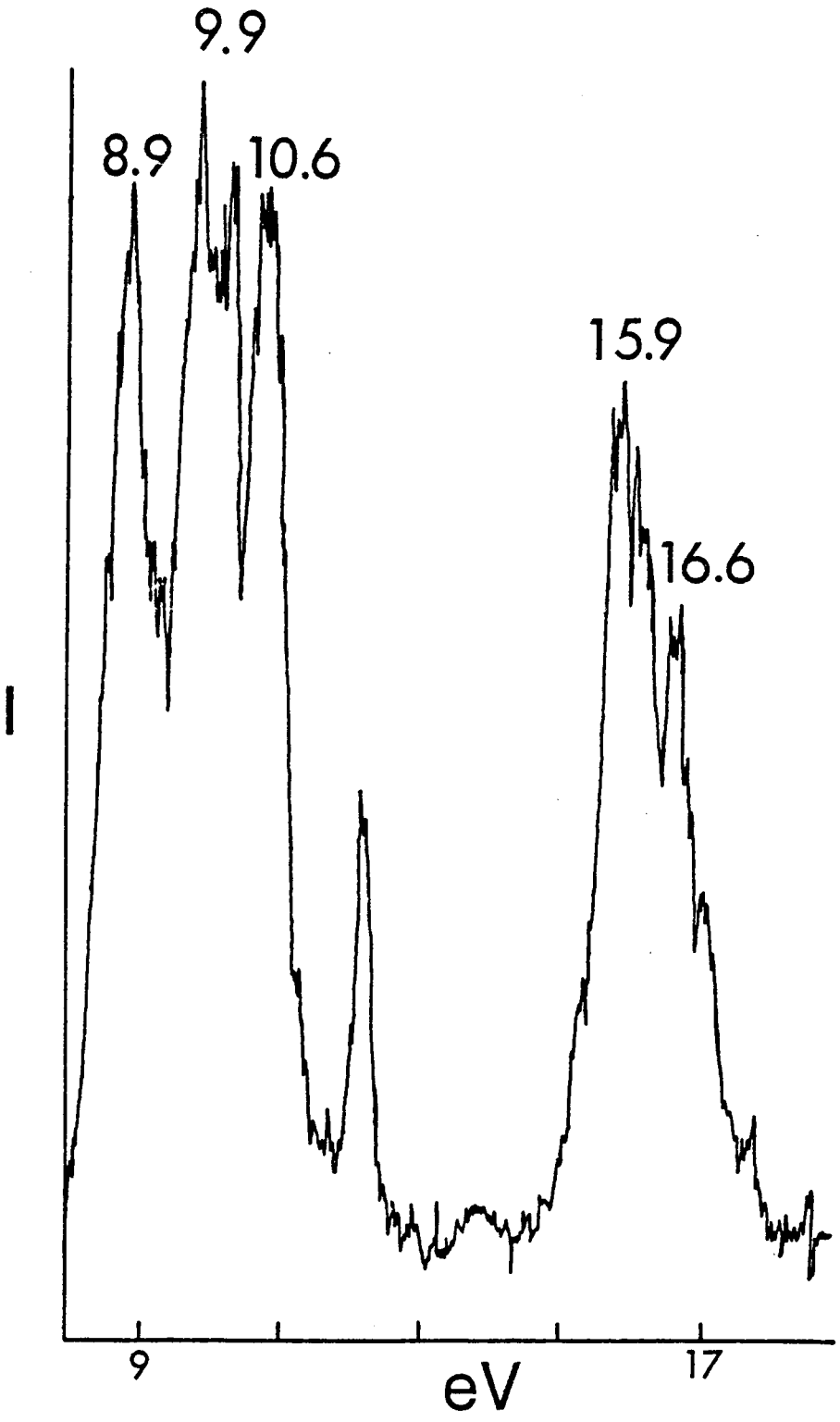

Figure 2. He(I) photoelectron spectrum of $RbNO_3$ vapor.

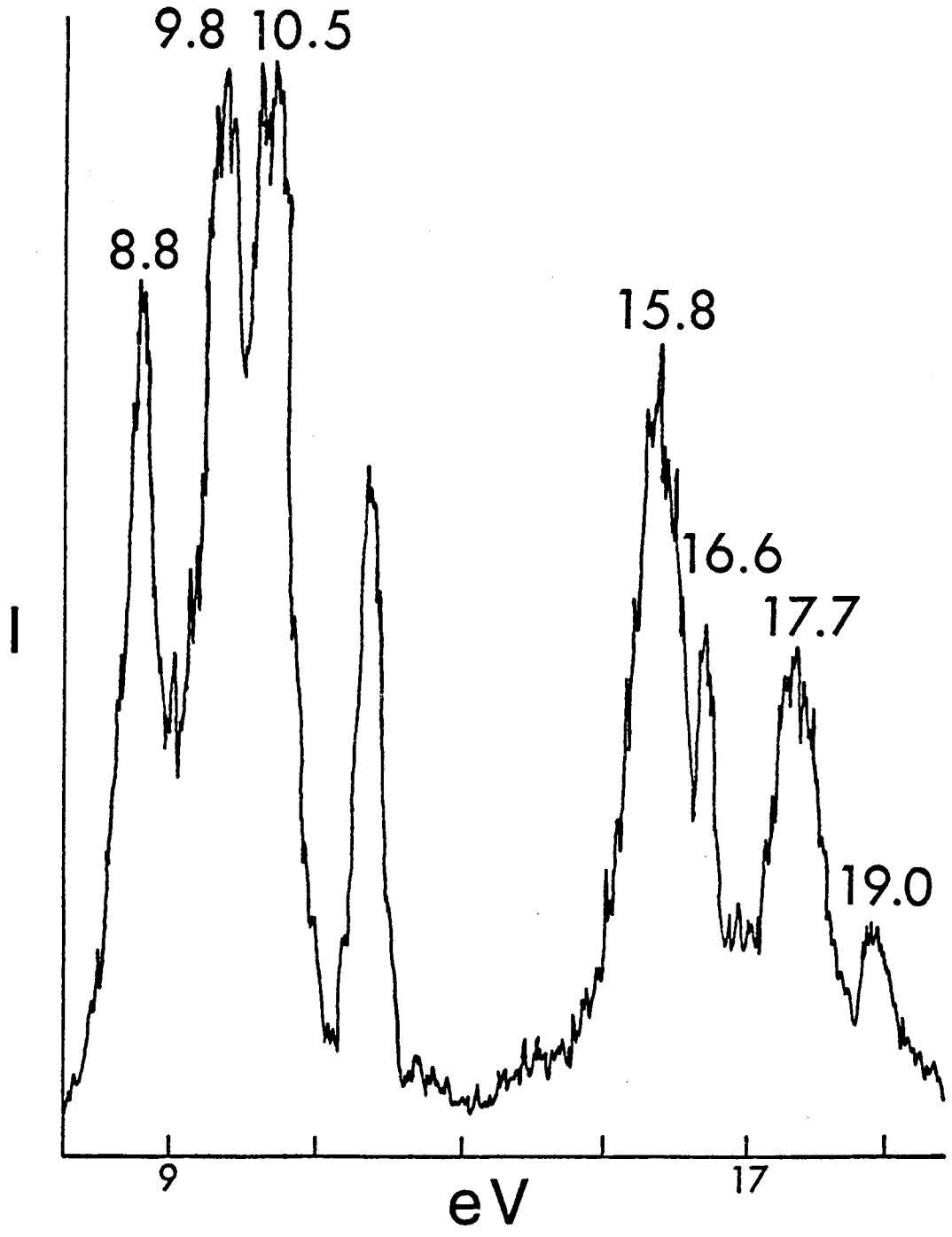

Figure 3. He(I) photoelectron spectrum of $CsNO_3$ vapor.

TABLE I

NITRATE EXPERIMENTAL IONIZATION ENERGIES (-eV)

KNO_3 (exp.)	$RbNO_3$ (exp.)	$CsNO_3$ (exp.)
8.96 ± 0.03[a]	8.89 ± 0.03[a]	8.78 ± 0.06[a]
9.94 ± 0.03	9.91 ± 0.04	9.84 ± 0.04
10.52 ± 0.03	10.59 ± 0.04	10.46 ± 0.04
16.13 ± 0.03	15.86 ± 0.04	15.76 ± 0.04
16.72 ± 0.03	16.57 ± 0.04	16.63 ± 0.07
		17.66 ± 0.07
		18.99 ± 0.07

[a]95 percent confidence limits.

from all spectra obtained and are characterized by the indicated 95 percent confidence limits.

When $LiNO_3$ and $NaNO_3$ were heated, the spectra obtained included characteristic lines due to N_2O, NO, and N_2 of such intensities as to suggest that N_2O, NO, and to a lesser extent N_2 had been evolved indicating the decomposition of both compounds. This is reasonable on the basis of vapor studies which have shown various decomposition products for metal nitrates with NO probably being predominant at high temperatures.[16] (The reaction usually given is $2MNO_3 \rightarrow M_2O + 2NO + {}^3/_2\, O_2$.) It is possible that total decomposition did not occur as small peaks perhaps due to metal nitrate were observed in the case of $NaNO_3$ but these were less intense than the N_2O and NO peaks and were partially masked by them. It is thus reasonable to assume that, at least in the case of $NaNO_3$, total decomposition does not occur. For $LiNO_3$ indications were that essentially complete decomposition took place, there being little evidence that $LiNO_3$ vapor was being produced in any appreciable quantity.

E. Interpretive Tools

The high-temperature stabilities and volatilities of all the alkali metal nitrates as well as thallium nitrate have been studied by various vapor-phase techniques. There is, however, conflicting reportage on decomposition of almost all the compounds. No doubt this is because the onset of decomposition is difficult to determine as it seems to be affected by pressure, composition of the atmosphere, the material of the sample container (and perhaps its construction), and the presence

of impurities, especially water. The nitrates of Li, Na, K, Rb, and Cs appear to be stable under certain conditions up to about 700°K, 750°K, 800°K, 800°K, and 800°K respectively, but reports are in conflict concerning the exact onset, degree, and rate of decomposition, particularly in the cases of $LiNO_3$ and $NaNO_3$.[17] Hardy and Field[18] have reported that anhydrous Li, Na, K, Rb, and Cs nitrates can all be slowly and smoothly distilled under a 0.05-torr vacuum at temperatures of 753°K, 723°K, 723°K, 723°K, and 773°K respectively without appreciable decomposition.

The mass spectrum of the vapors over $LiNO_3$ at 673°K as obtained by Büchler and Stauffer[19] indicates the presence of about equal amounts of monomer and dimer along with smaller amounts of decomposition products (O_2, NO, N_2), whereas the mass spectrum of $NaNO_3$ at 750°K suggests considerable decomposition although the dimer/monomer ratio was still approximately unity.[19] Lauden, Towler, and Wuth[20] have obtained the mass spectrum of the vapors above molten $RbNO_3$ at 720°K and above molten $CsNO_3$ at 643°K. Their findings indicate that the vapor in each case is almost all monomer with only a few percent dimer and no decomposition products. However, in a similar study[21] of $CsNO_3$ at 775°K slight decomposition was detected. In addition, the mass spectrum of $T\ell NO_3$[22] in the temperature range 513-613°K indicates the predominance of monomer in the vapor with small amounts of dimer and some thermal decomposition products, principally NO and N_2O.

Infrared data have been obtained for all of these compounds. Smith, James, and Devlin[23] have isolated vapors of $LiNO_3$, $NaNO_3$, KNO_3, and $RbNO_3$ in noble gas matrices and have obtained their infrared spectra. Assignments of bands were made on the basis of a trigonal planar NO_3^-

ion with the metal cation bidentate between two oxygens (C_{2v}). Other bands were assigned to the dimer molecule for which Smith et al.[23] have proposed an eight-membered ring structure └M-O-NO-O-M-O-NO-O┘. Smyrl and Devlin[24] and Jacox and Milligan[25] obtained similar results in their matrix-isolation infrared studies of $LiNO_3$ and KNO_3. Shapovalov, Shevel'kov, and Mal'tsev[26] have studied the infrared spectra of the vapors over $CsNO_3$ and $T\ell NO_3$. Bands were assigned on the basis of a C_{2v} structure with a bidentate metal atom bridging two oxygen atoms of a trigonal planar nitrate group, but because a band associated with M-O bonding was not seen definite assignments could not be assured.

Khodchenkov et al.[27] obtained electron diffraction data for the vapors above $LiNO_3$ and $NaNO_3$ in the temperature range 723-777°K and concluded that they best fit structural parameters characteristic of a monodentate-type molecule, a conclusion which later experiments on $T\ell NO_3$[28] and some other oxyanion-containing compounds have called into question. The authors concluded further that their data analysis procedure was inadequate and stated that a more sophisticated program would subsequently be employed. The electron diffraction results obtained for $T\ell NO_3$ vapors[28] have been fit by assuming a superposition of three $T\ell NO_3$ models: a C_s molecule with a planar triangular nitrate and the Tℓ attached to one oxygen, a C_{2v} molecule with a planar triangular nitrate and the Tℓ bridging two oxygens, and a C_{3v} molecule with a planar triangular nitrate and the Tℓ above the nitrate to form a pyramid. The combination which fits the data best is 11 percent C_s, 71 percent C_{2v}, and 18 percent C_{3v}. The authors also considered a dynamic model in which the $T\ell^+$ and NO_3^- were viewed as continually moving with respect

to each other or in which the $T\ell^+$ is viewed as belonging to all the ligand oxygens with equal probability (the so-called polytopic bond). In view of these data and the infrared spectroscopic results the monomer alkali nitrate molecule is probably best thought of as having a C_{2v} structure with the alkali metal ion occupying a bidentate bridging position between two oxygen atoms of the trigonal planar nitrate group.

Rambidi[29] has employed a simple electrostatic model to examine the potential energy surfaces associated with the distribution of the Cs^+ cation about the NO_3^- anion in $CsNO_3$ vapor. He has concluded that the nature of the bonding at high temperatures is polytopic in that large displacements of the Cs^+ in a plane normal to the NO_3^- group can be brought about by small variations in the total system energy. This behavior may be characteristic of other nitrates as well as other oxyanion-containing compounds.

Theoretical MO calculations for the free nitrate ion have been carried out by several means including ab initio approaches.[30-33] The results of the ab initio calculations are summarized in Table II (p 22). Upon examination of the theoretical MO data the outer MOs (molecular orbitals) ($1a_2'$, 1e", 4e') are found to be predominantly composed of O2p AOs (atomic orbitals), the next two MOs (3e', $1a_2$") have strong contributions from both the O2p and N2p AOs, and the $4a_1'$ MO has N2s, O2s, and O2p as its major AO (atomic orbital) contributors. In addition to these theoretical results, X-ray photoelectron data are available for solid $LiNO_3$, $NaNO_3$, and KNO_3.[34] He(II) photoelectron data are available for solid KNO_3,[33] and He(I) photoelectron data are available for $T\ell NO_3$ vapor[13] and $F_3C\text{-}Hg\text{-}ONO_2$ vapor.[35] The results of the experimental work

TABLE II

MO CALCULATIONS FOR NO_3^- (-eV)

MO	Ab Initio[a]	Ab Initio[b]	Ab Initio[c]	Ab Initio[d]	Ab Initio[e]
$1a_2'$	9.9	9.9	9.9	9.9	9.9
1e"	10.1	10.1	10.0	10.4	9.9
4e'	11.4	11.6	11.4	11.9	11.4
3e'	17.7	17.8	17.5	17.6	17.5
$1a_2"$	18.9	18.8	19.3	19.1	18.1
$4a_1'$	20.5	20.5	19.6	19.8	20.7

[a]Ref. 30, adjusted by Q = -4.1 eV.

[b]Ref. 32, adjusted by Q = -4.1 eV.

[c]Ref. 31, without d orbitals, adjusted by Q = -5.1 eV.

[d]Ref. 31, with d orbitals, adjusted by Q = -5.5 eV.

[e]Ref. 33, adjusted by Q = -3.6 eV.

are presented in Table III (p 24). Upon examination of the He(I) and He(II) spectra the intensities of the a_2'' lines are found to be considerably less than those of the a_2', e', and e" lines.

For the present work UTARC (an extended Hückel method) calculations have been carried out on KNO_3 and on the NO_3^- ion with various structural parameter alternations. Computations have been made on KNO_3 in C_{3v} structures, C_{2v} bidentate configurations, C_{2v} monodentate configurations, and in C_s configurations, all subjected to variations in both the O-N-O angles and the K-N distances. Computations have also been made on the NO_3^- ion with appropriate alterations in the O-N-O angles. The purpose of these computations was to observe the changes in MO orbital levels and the splittings of MO levels when bond angle and bond length alterations were made. The results of selected calculations are presented in Table IV (p 25) where the shifts and splits have been imposed upon the ab initio MO values. The data may be taken to indicate that small changes in the O-N-O angles or substantial changes in the K^+ position or both do not strongly affect the MO energy values, leaving the ordering unchanged. Changes in the K-N distance have similar small effects. In all these changes the dissolution of the D_{3h} symmetry of the NO_3^- results in only very small MO splits, usually no more than a few tenths of an eV.

F. Conclusions

Comparisons of the energy values of the bands of Figures 1-3 (pp 14-16) have been made with the ab initio MO calculations of Table II (p 22) (altered by subtraction of 0.9-1.0 eV), the X-ray PES results

TABLE III

EXPERIMENTAL RESULTS ON NITRATES (-eV)

MO	Solid MNO_3 X-ray[a]	Solid KNO_3 He(II)[b]	Vapor F_3C-Hg-ONO_2 He(I)[c]	Vapor $T\ell NO_3$ He(I)[d]
$1a_2'$	10.8	9.9	11.1	9.9
$1e''$		(10.8)[e]	12.1	11.1
$4e'$		(11.6)[e]	12.6	11.4
$3e'$	17.2	16.8	--[f]	16.7
$1a_2''$		17.4	--[f]	17.2
$4a_1'$	19.8	19.5	--[f]	--

[a]Ref. 34.

[b]Ref. 33.

[c]Ref. 35.

[d]Revised interpretation of spectrum in ref. 13, with line at 14.2 eV being assigned to a decomposition product.

[e]Values obtained by deconvolution.

[f]Obscured by F_3C-lines.

TABLE IV

NO_3^- AND KNO_3 SHIFT AND SPLIT CALCULATIONS (-eV)[a]

	Entity	MOs and Energies (-eV)[a]							
D_{3h}	NO_3^- anion	$1a_2'$	1e"	1e"	4e'	4e'	3e'	3e'	$1a_2$"
	N-O(1.22A)	9.0	9.2	9.2	10.6	10.6	16.7	16.7	17.9
	O-N-O(120°)								
C_{2v}	NO_3^- anion	$4b_2$	$1a_2$	$2b_1$	$3b_2$	$5a_1$	$2b_2$	$4a_1$	$1b_1$
	N-O(1.22A)	9.0	9.2	9.5	10.7	10.8	16.8	16.8	17.9
	O-N-O(115°)								
C_{2v}	NO_3^- anion	$4b_2$	$1a_2$	$2b_1$	$3b_2$	$5a_1$	$2b_2$	$4a_1$	$1b_1$
	N-O(1.22A)	9.0	9.4	10.1	11.2	11.5	17.0	17.3	18.4
	O-N-O(105°)								
C_{3v}	$K^+NO_3^-$ pyramidal	$1a_2$	5e	5e	4e	4e	3e	3e	$4a_1$
	N-O(1.22A)	9.0	9.6	9.6	11.3	11.3	18.1	18.1	19.0
	K-N(1.82A)								
C_{3v}	$K^+NO_3^-$ pyramidal	$1a_2$	5e	5e	4e	4e	3e	3e	$4a_1$
	N-O(1.22A)	9.0	9.6	9.6	11.2	11.2	17.8	17.8	18.8
	K-N(2.22A)								
C_{3v}	$K^+NO_3^-$ pyramidal	$1a_2$	5e	5e	4e	4e	3e	3e	$4a_1$
	N-O(1.22A)	9.0	9.5	9.5	11.1	11.1	17.6	17.6	18.7
	K-N(2.62A)								
C_{2v}	$K^+NO_3^-$ bidentate	$4b_2$	$2b_1$	$1a_2$	$5a_1$	$3b_2$	$4a_1$	$2b_2$	$1b_1$
	N-O(1.22A)	9.0	9.3	9.5	11.2	11.2	17.7	17.8	18.6
	K-N(2.42A)								
C_{2v}	$K^+NO_3^-$ bidentate	$4b_2$	$2b_1$	$1a_2$	$5a_1$	$3b_2$	$4a_1$	$2b_2$	$1b_1$
	N-O(1.22A)	9.0	9.4	9.5	11.2	11.2	17.6	17.7	18.6
	K-N(2.82A)								
C_{2v}	$K^+NO_3^-$ bidentate	$4b_2$	$2b_1$	$1a_2$	$5a_1$	$3b_2$	$4a_1$	$2b_2$	$1b_1$
	N-O(1.22A)	9.0	9.4	9.4	11.1	11.2	17.4	17.5	18.5
	K-N(3.22A)								
C_{2v}	$K^+NO_3^-$ monodentate	$4b_2$	$1a_2$	$2b_1$	$3b_2$	$5a_1$	$2b_2$	$4a_1$	$1b_1$
	N-O(1.22A)	9.0	9.4	9.6	11.6	11.7	17.8	18.1	19.1
	K-N(3.22A)								
C_s	$K^+NO_3^-$ monodentate	5a"	4a"	7a'	3a"	6a'	2a"	5a'	4a'
	N-O(1.22A)	9.0	9.3	9.5	11.4	11.5	17.8	18.1	19.1
	K-N(3.19A)								
	N-O-K(105°)								

[a]All values adjusted to first MO = 9.0 eV.

on solid MNO_3 compounds[34] of Table III (p 24) (altered by subtraction of 0.9 eV), the He(II) PES results on solid KNO_3[33] (altered by subtraction of 0.9 eV), the He(I) PES results on $F_3C\text{-}Hg\text{-}ONO_2$ vapor[35] (altered by subtraction of 2.1 eV), and with the He(I) PES results on $T\ell NO_3$ vapor[13] (altered by subtraction of 0.9 eV). Comparisons of the bands of Figures 1-3 (pp 14-16) have also been made with band areas and shapes of the He(II) solid KNO_3 spectrum,[33] the He(I) $F_3C\text{-}Hg\text{-}ONO_2$ spectrum,[35] the He(I) $T\ell NO_3$ spectrum,[13] and with spectra of neutral D_{3h} compounds such as those of BF_3,[36] $BC\ell_3$,[36] BBr_3,[36] BI_3,[36] and SO_3.[37] The spectra of solid KNO_3, gaseous $F_3C\text{-}Hg\text{-}ONO_2$, gaseous $T\ell NO_3$, BF_3, $BC\ell_3$, BBr_3, BI_3, and SO_3 are presented as Figures 4-8 (pp 27-30) for comparison. In addition the experimental values for each are given in Tables III (p 24) and V (p 31). It has been concluded that the energy order in each of the three vapors (KNO_3, $RbNO_3$, $CsNO_3$) is $1a_2'$, 1e", 4e', 3e', $1a_2"$. It needs to be recognized that this ordering has been based on calculations on ground-state entities and that therefore relaxation has not been taken into direct consideration. This is also the situation in the cases of the other D_{3h} molecules mentioned above. Relaxations for the delocalized or bonding MOs can often be estimated from the constituent AO contributions, but relaxations from localized MOs are somewhat more difficult to estimate particularly because of the electron flow considerations.[38] The outer three MOs ($1a_2'$, 1e", 4e') are localized ones and therefore it is they that might need to be reordered in light of relaxational phenomena. It is to be noted that the ordering of the 1e" and 4e' MOs is still uncertain in the BX_3 compounds, there being a good possibility that considerable interaction between the two may be occurring.[39]

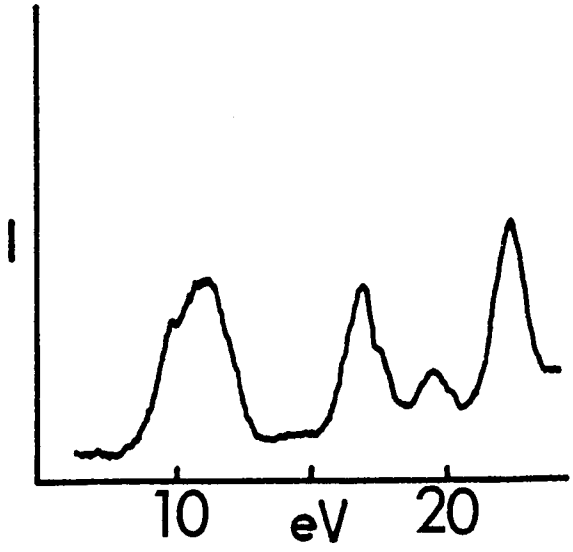

Figure 4. He(II) photoelectron spectrum of solid KNO_3.

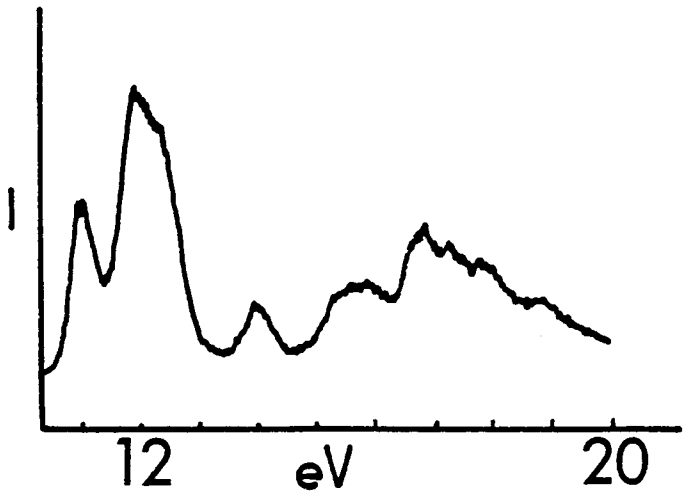

Figure 5. He(I) photoelectron spectrum of F_3C-Hg-ONO_2.

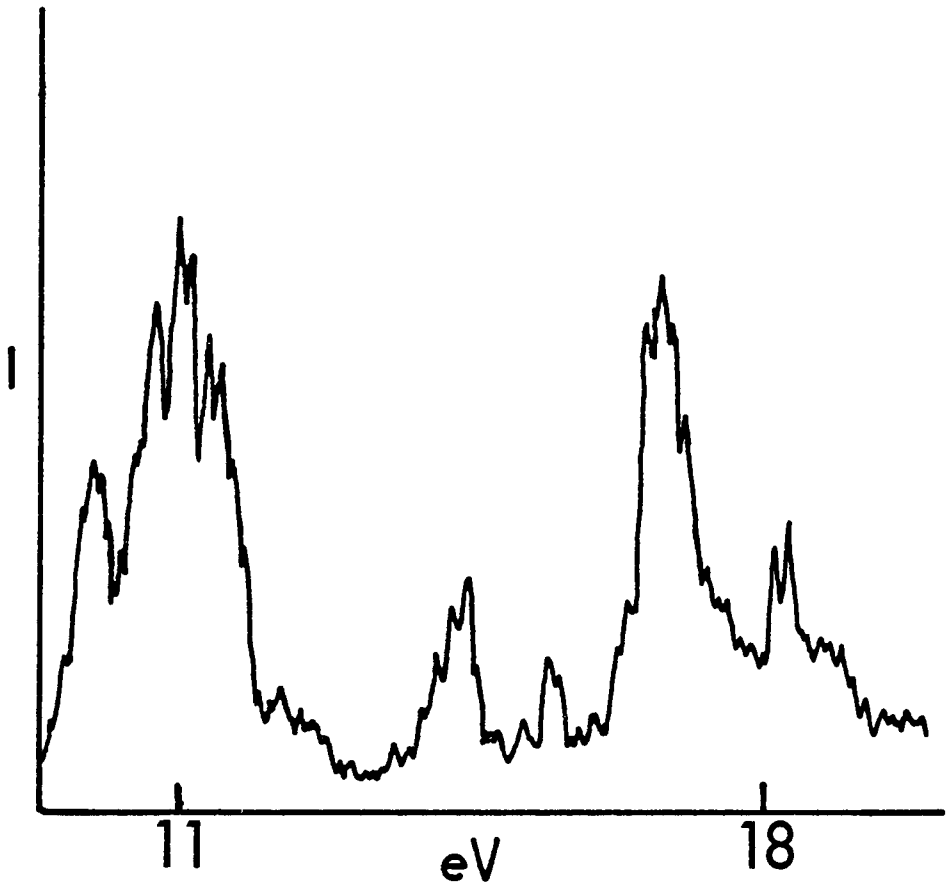

Figure 6. He(I) photoelectron spectrum of $T\ell NO_3$ vapor.

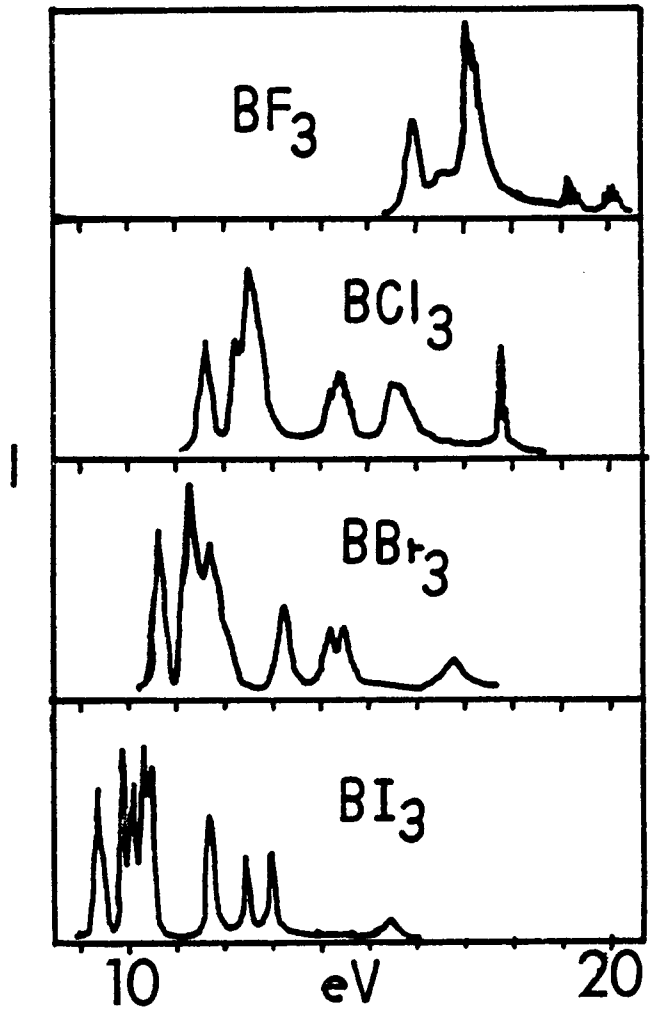

Figure 7. He(I) photoelectron spectra of BF_3, $BC\ell_3$, BBr_3, and BI_3.

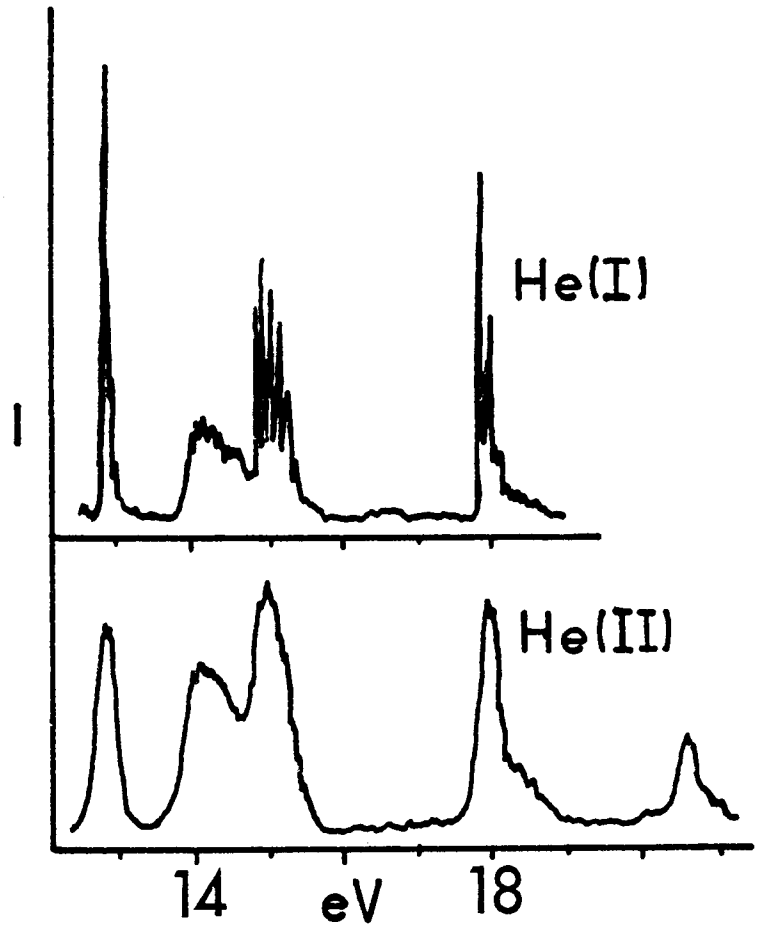

Figure 8. He(I) and He(II) photoelectron spectra of SO_3.

TABLE V

EXPERIMENTAL He(I) DATA ON NEUTRAL D_{3h} COMPOUNDS

MO	BF_3[a]	$BC\ell_3$[a]	BBr_3[a]	BI_3[a]	SO_3[b]
$1a_2'$	15.95 (15.95)	11.73 (11.62)	10.65 (10.65)	9.36 (9.36)	12.8
1e"	16.67 (17.10)	12.39 (12.53)	11.36 (11.36)	9.92 (9.92) 10.10 (10.10)	14.1
4e'	17.14 (16.65)	12.66 (12.28)	11.71 (11.71)	10.36 (10.36) 10.48 (10.48)	15.0
3e'	20.09 (20.10)	15.54 (15.49)	14.20 (14.20) 14.46 (14.46)	12.46 (12.46) 12.96 (12.96)	17.9
$1a_2"$	19.13 (19.15)	14.42 (14.35)	13.18 (13.18)	11.74 (11.74)	18.0

[a]Ref. 36. Values shown in parentheses are from another investigator in Ref. 36. These are given to indicate the uncertainty of the assignments.

[b]Ref. 37.

The first three MOs ($1a_2'$, 1e", 4e') are largely O2p in character, the $1a_2'$ and 1e" being entirely non-bonding and the 4e' being slightly N-O bonding by virtue of a small percentage of N2p AO. Unlike the He(II) data on solid KNO_3[33] and the He(I) data on gaseous $F_3C\text{-}Hg\text{-}ONO_2$,[35] the 1e" and 4e' ionizations are resolved (as they are in gaseous SO_3,[37] $BC\ell_3$,[36] BBr_3,[36] BI_3,[36] and $T\ell NO_3$[13]). The splittings which sometimes can be seen in the 1e" and 4e' ionizations (note the 9.9 eV peak in Figure 2 (p 15), the 9.8 eV and 10.5 eV peaks in Figure 3 (p 16), and the 11.1 eV and 11.4 eV peaks in the $T\ell NO_3$ spectrum[13]) may be actual, but they cannot be consistently reproduced. This may be due to the variability of the resolution in the high-temperature experiments.

The next two bands originate from the 3e' and the $1a_2$" MOs. These orbitals are principally N-O bonding ones. Again the bands are resolved, unlike the situation in the He(II) spectrum of solid KNO_3.[33] In the spectrum of $CsNO_3$ (Figure 3, p 16) the 6th and 7th bands (at 17.7 and 19.0 eV) are assigned to the $5^2P_{3/2}$ and $5^2P_{1/2}$ states of Cs^{++}. These assignments are analogous to those of Potts and Williams[40] for the gaseous cesium halides as exemplified in Figure 9 (p 33) and to those of Vick et al.[14] for gaseous $CsReO_4$ as shown in Figure 10 (p 34).

In all the spectra (solid KNO_3,[33] gaseous KNO_3, gaseous $RbNO_3$, gaseous $CsNO_3$, gaseous $T\ell NO_3$,[13] gaseous $BC\ell_3$,[36] gaseous BBr_3,[36] gaseous BI_3,[36] gaseous SO_3,[37] gaseous $F_3C\text{-}Hg\text{-}ONO_2$[35]) the bands are generally quite broad. These breadths may be associated with a number of factors (symmetry-dissolution of the D_{3h} NO_3^- group by attached entities in the cases of the nitrates, Jahn-Teller effects in the ionization of degenerate levels in all entities, differences in the potential energy

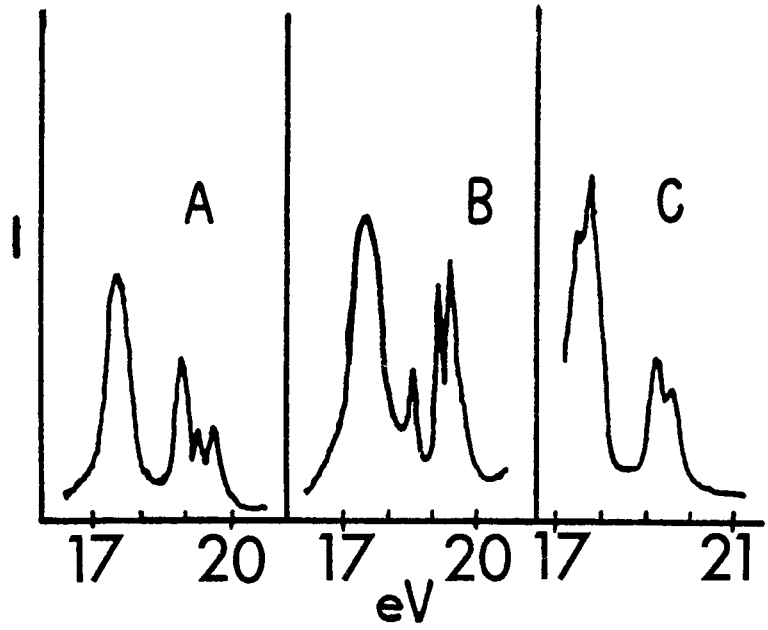

Figure 9. Cesium regions of the He(II) photoelectron spectra of (A) CsCℓ, (B) CsBr, and (C) CsI.

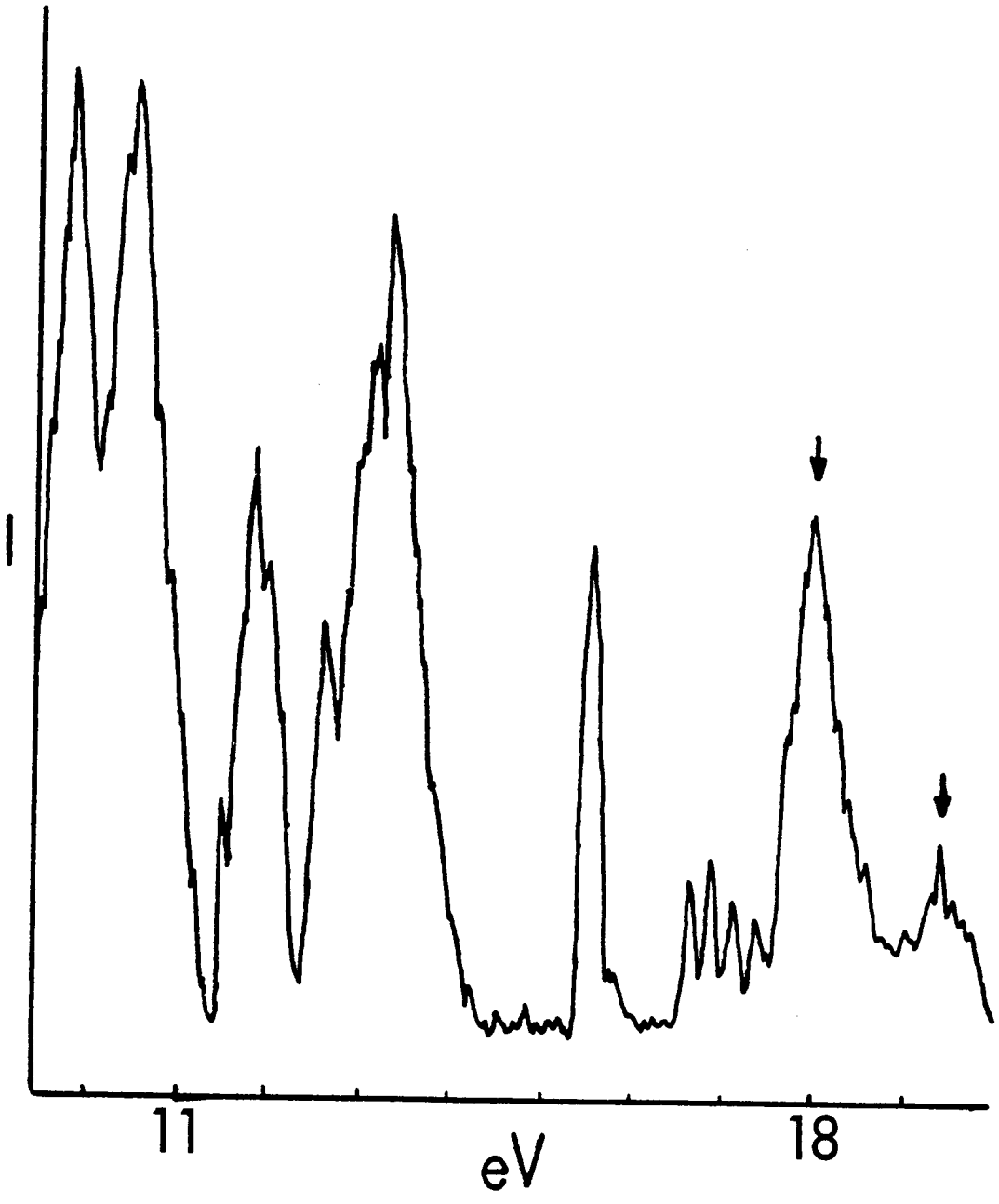

Figure 10. He(I) photoelectron spectrum of $CsReO_4$ vapor with cesium bands indicated by arrows.

surfaces between the un-ionized original entity and the ionized entity, thermal excitation of vibrational modes, and banding in the solids). In all the nitrate compounds whether solid or gaseous, whether covalent or ionic, whether room-temperature or high-temperature, the bands show strong similarities in shapes, breadths, and positions. And further, they all resemble the SO_3 spectrum[37] with the energy envelope of the five outer occupied MOs compressed. All of these observations may be taken to indicate that the NO_3^- entity has considerable symmetry integrity, being perturbed only minimally by variations in external influence. Such an inference is in agreement with the calculational results in Table IV (p 25). Any hope of distinguishing between C_{3v}, C_{2v}, and C_s forms of the gaseous $M^+NO_3^-$ molecules is dissolved by the small splits produced by perturbations, by the observed band breadths, and by the instrumental resolution which is no better than 0.15 eV at high temperatures (largely due to sample deposition on the walls of the sample chamber and on the slits). Neither can a judgment be made concerning the polytopicity of the vapor-state $M^+NO_3^-$ molecules.[29,41]

CHAPTER III

THE ALKALI METAPHOSPHATES

A. Abstract

The He(I) photoelectron spectra of the gaseous metaphosphates of Na, K, Rb, and Cs have been obtained using a modified high-temperature cylindrical-mirror electron spectrometer equipped with a resistance-heated sample oven. Attempts to acquire data for $LiPO_3$ have been unsuccessful because of the extremely high temperature required, on the order of 1400°K. The identities of the vapor-phase molecules were based on mass spectrometric data and the spectral lines were assigned molecular orbital origins through the use of MO calculations and analogies to other ionic compounds of similar types, particularly the alkali nitrates.

B. Introduction

Mass spectrometric results on the composition of the vapors above heated alkali metal metaphosphates indicate the monomer MPO_3 to be the stable predominant gaseous species in all cases with only a very small amount of dimer present in any case. Based on these studies attributing stability to the MPO_3 vapor molecules and analogies to the alkali metal nitrates, this present study was undertaken to obtain the UPES spectra for these vapor compounds.

C. Experimental Procedure

Spectral measurements were made with a modified truncated cylindrical-mirror analyzer which has been described previously.[11] The spectrometer was equipped with a resistance-heated tantalum-strip-wound quartz cell for the volatilization of the alkali metaphosphates. The cell was coated with a high-temperature ceramic cement and was heated by a 0-12 volt AC power supply. The procedures for sample handling and spectral accumulation have also been described previously[13] and will not be repeated here.

$LiPO_3$ was obtained from Pfaltz and Bauer, $NaPO_3$ was purchased from Matheson (MCB), and KPO_3 was acquired from Research Organic/Inorganic Chemical Corporation. Except for drying, they were used as obtained. Rubidium metaphosphate and cesium metaphosphate were prepared by the in situ dehydration of RbH_2PO_4 and CsH_2PO_4 which were obtained from K & K Laboratories, a division of ICN Pharmaceuticals.

D. Results

The He(I) photoelectron spectra of the vapors above heated $NaPO_3$, KPO_3, $RbPO_3$, and $CsPO_3$ are presented as Figures 11-14 (pp 38-41). Each is a typical spectrum chosen from 20 or more spectra obtained for each compound. The spectral peaks for each compound are labeled with the average experimental ionization energy values (rounded to one decimal). Unnumbered peaks which are designated by the letters Ar and W are due to argon and water, respectively, used as calibrants. The values assigned to the peaks for each compound are listed in Table VI (p 42).

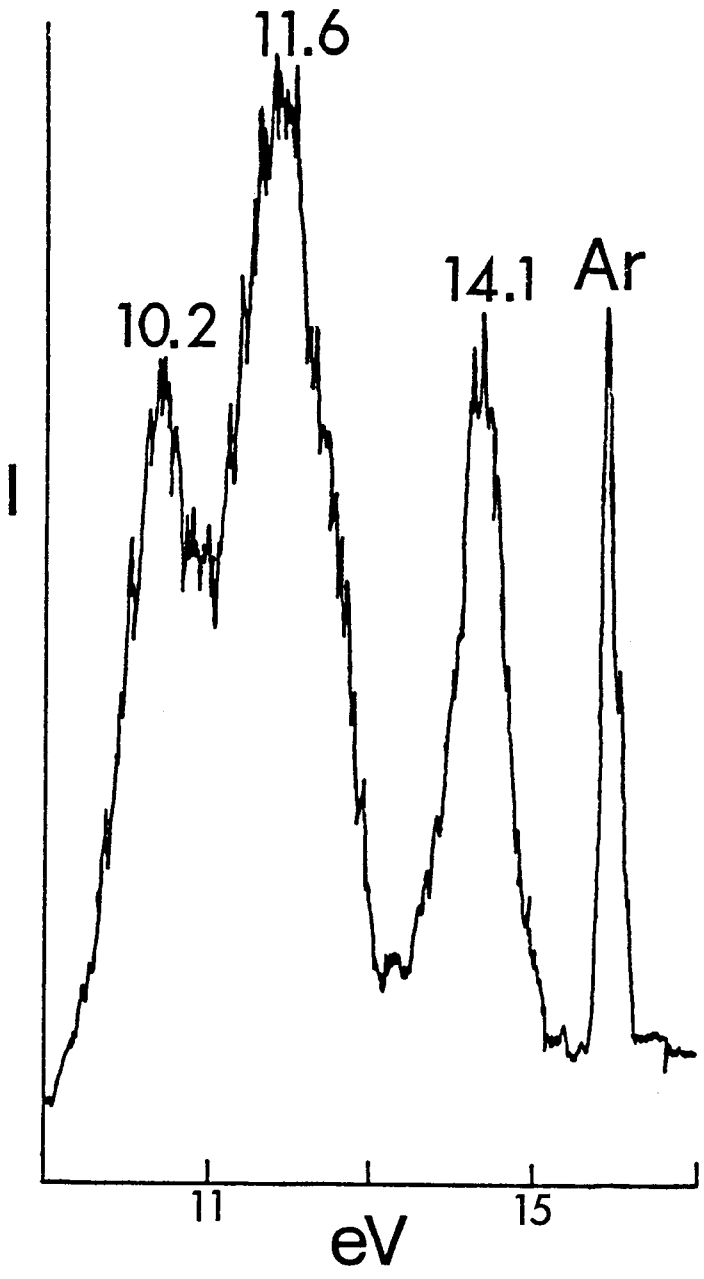

Figure 11. He(I) photoelectron spectrum of $NaPO_3$ vapor.

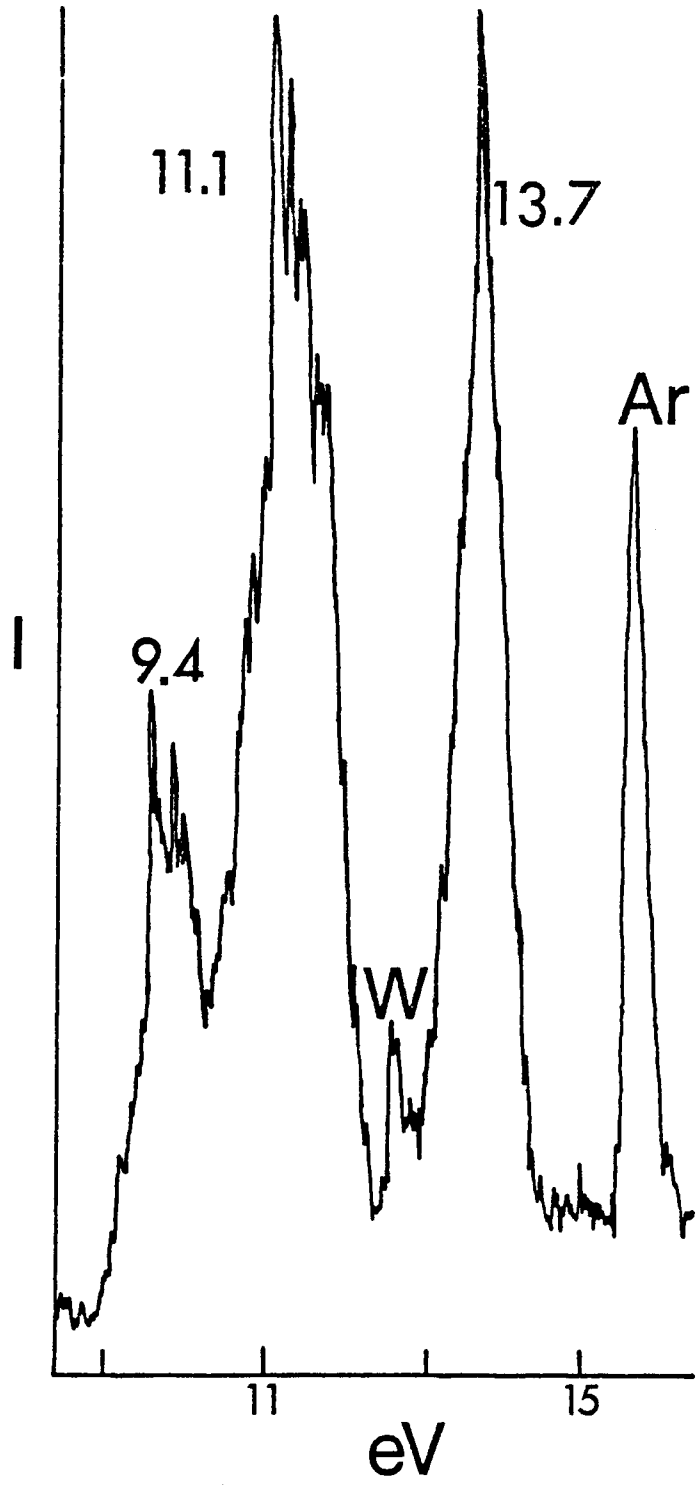

Figure 12. He(I) photoelectron spectrum of KPO_3 vapor.

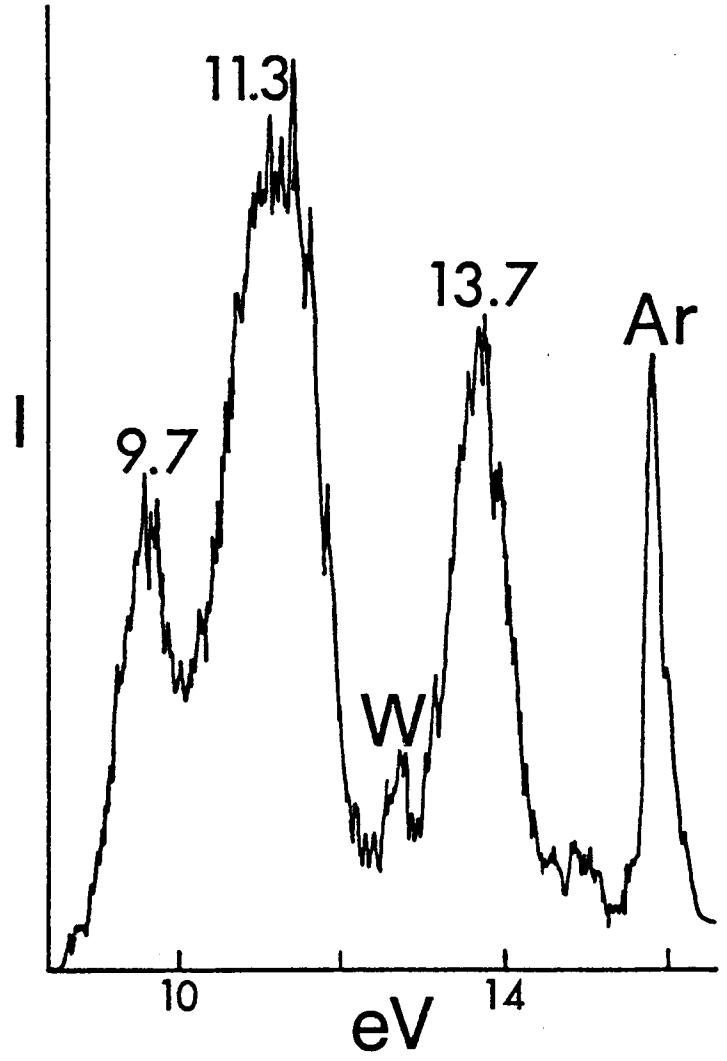

Figure 13. He(I) photoelectron spectrum of $RbPO_3$ vapor.

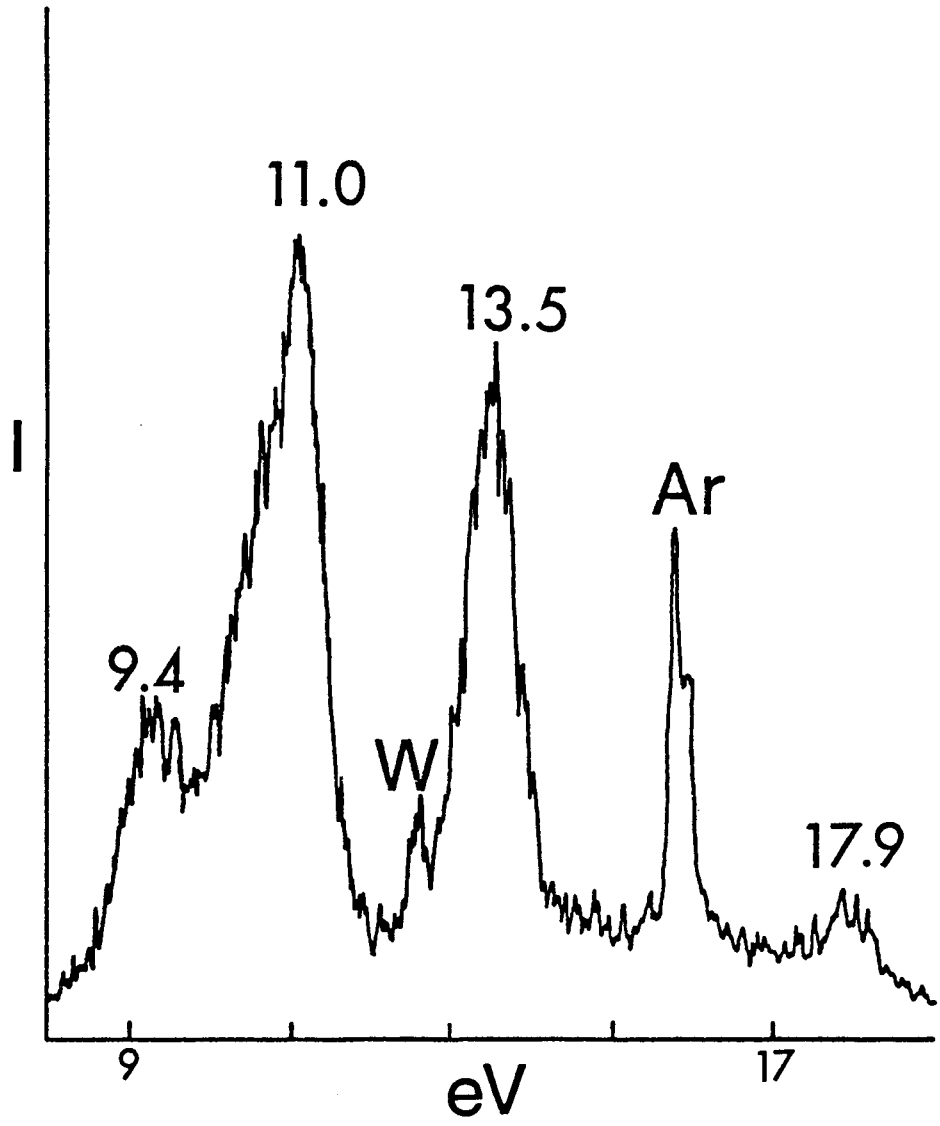

Figure 14. He(I) photoelectron spectrum of $CsPO_3$ vapor.

TABLE VI

METAPHOSPHATE EXPERIMENTAL IONIZATION ENERGIES (-eV)

$NaPO_3$ (exp.)	KPO_3 (exp.)	$RbPO_3$ (exp.)	$CsPO_3$ (exp.)
10.16 ± 0.04[a]	9.44 ± 0.03[a]	9.70 ± 0.04[a]	9.41 ± 0.04[a]
11.58 ± 0.04	11.09 ± 0.06	11.27 ± 0.03	10.99 ± 0.03
14.14 ± 0.02	13.70 ± 0.03	13.71 ± 0.03	13.48 ± 0.02
			17.85 ± 0.02

[a]95 percent confidence limits.

These values are the unweighted averages of the values taken from all spectra obtained and are followed by the characterizing 95 percent confidence limits.

Many attempts were made to accumulate spectral data on gaseous $LiPO_3$ but no success was achieved. Volatilization of the compound was complicated by metaphosphate attack on the quartz cell and high-temperature oxidation of the tantalum heating strip. Boron nitride was used as a substitute for the quartz and, although no attack on the container was detected, oxidation of the tantalum strip again limited the results. In several instances small peaks began to arise in the regions expected from the data on the other alkali metaphosphates, but these were never of sufficient statistical significance to report as valid results.

E. Interpretive Tools

The high-temperature stabilities and volatilities of all the alkali metaphosphates have been determined by several mass spectrometric investigations. Lithium metaphosphate has been found to sublime and evaporate predominantly to the monomer in the region of 940-1389°K.[42] Sodium metaphosphate also vaporizes predominantly to the monomer with only small amounts of dimer; at 1337°K, $pNaPO_3(g) = 1.3 \times 10^{-1}$ torr.[43,44] In the region 1050-1298°K, KPO_3 exhibits similar behavior,[45,46] with $pKPO_3(g) = 1.7 \times 10^{-2}$ torr at 1180°K, as does $RbPO_3$ in the region 1142-1308°K.[47] A general mass spectrometric study of all the alkali metaphosphates by Alikhanyan *et al.*[48] indicates that the monomer MPO_3 is the strongly predominant stable vapor species in all cases with only negligible amounts of dimer in any case. For Li, Na, K, Rb, and Cs

metaphosphates the temperatures at which partial pressures of 10^{-2} torr were indicated are 1288°K, 1202°K, 1175°K, 1163°K, and 1093°K, respectively. Another investigation of the thermal stability of the alkali metaphosphates by the Knudsen effusion method and mass spectrometric analyses of the vaporization products yielded similar results.[49] In addition, electron-impact appearance potentials were obtained for the $LiPO_3^+$, $NaPO_3^+$, and $CsPO_3^+$ ions of approximately 9.6 eV, 9.1 eV, and 8.9 eV respectively.[49]

The alkali metaphosphates have not been subjected to other types of vapor study such as electron diffraction, infrared spectroscopy, or Raman spectroscopy. It is, however, reasonable to assume that results similar to those obtained for the alkali nitrates might be observed. These results have been discussed in Chapter II.

Theoretical ab initio molecular orbital calculations for the free metaphosphate ion have recently been reported by Loew and MacArthur.[31] Computations, both including and excluding the phosphorus d orbitals, have been carried out. These are summarized in Table VII (p 45). UTARC (an extended Hückel method) results for the free PO_3^- anion are also given in Table VII (p 45).

F. Conclusions

In Table VIII (p 46) the experimental results for the metaphosphates are compared to the results for the alkali nitrates, and molecular orbital assignments are presented. These assignments have been made on the following bases. Comparison of the bands of Figures 11-14 (pp 38-41) were made with band shapes and positions of the gaseous alkali

TABLE VII

MO CALCULATIONS FOR PO_3^- (-eV)

MO	Ab Initio[a]	Ab Initio[b]	UTARC[c]
$1a_2'$	9.4	9.4	9.4
1e"	9.3	10.1	9.8
4e'	9.7	10.7	10.0
3e'	13.0	13.2	11.4
$1a_2"$	13.7	13.3	12.2
$4a_1'$	16.4	16.5	15.3

[a]Ref. 31, without d orbitals, adjusted by Q = -3.7 eV.

[b]Ref. 31, with d orbitals, adjusted by Q = -4.0 eV.

[c]This paper, adjusted by Q = -1.1 eV.

TABLE VIII

EXPERIMENTAL IONIZATION ENERGY COMPARISONS (-eV)

Band:	1	2	3	4	5	6
$NaPO_3$	10.2	-- 11.6 --		-- 14.1 --		
KNO_3	9.0	9.9	10.5	16.1	16.7	
KPO_3	9.4	-- 11.1 --		-- 13.7 --		
$RbNO_3$	8.9	9.9	10.6	15.9	16.6	
$RbPO_3$	9.7	-- 11.3 --		-- 13.7 --		
$CsNO_3$	8.8	9.8	10.5	15.8	16.6	17.7, 19.0
$CsPO_3$	9.4	-- 11.0 --		-- 13.5 --		17.9
SO_3	12.8	14.1	15.0	17.9	18.0	
SO_3[a]	9.4	10.4	11.1	13.4	13.5	
BCl_3	11.6	12.5	12.3	15.5	14.4	
BCl_3[b]	9.4	10.3	10.1	13.3	12.2	
$AlCl_3$	12.0	12.7	12.5	14.0	13.3	
MO:	$1a_2'$	1e"	4e'	3e'	$1a_2"$	Cs 5p

[a]Adjusted by 0.8x + 0.7 eV.

[b]Adjusted by +2.2 eV.

nitrate He(I) spectra, the gaseous $T\ell NO_3$ He(I) spectrum,[13] and the solid KNO_3 He(II) spectrum,[33] Figures 1, 2, 3, 4, and 6 (pp 14, 15, 16, 27, and 28). Based on these comparisons and conclusions arrived at for the alkali nitrates in Chapter II, it is suggested that the energy level order in each of the four vapors ($NaPO_3$, KPO_3, $RbPO_3$, and $CsPO_3$) is $1a_2'$, 1e", 4e', 3e', $1a_2"$, the second-third and the fourth-fifth bands overlapping. In addition, PO_3^- is isoelectronic with SO_3[37] (Figure 8, p 30) and valence isoelectronic with the boron trihalides,[36] BF_3, $BC\ell_3$, BBr_3, and BI_3 (Figure 7, p 29). Experimental ionization energies for SO_3 and $BC\ell_3$ are presented for comparison in Table VIII (p 46). The molecular ordering is the same for SO_3 as in the above metaphosphate proposals. However, for $BC\ell_3$ there is a possible inversion in the ordering of the 1e" and 4e' molecular orbitals and a definitive change in the relative order of the 3e' and $1a_2"$ molecular orbitals. The question of a 1e"-4e' inversion is not yet resolved,[39] but, in any case, the two levels are very close in energy.

The valence bands for the metaphosphates compare well with the valence bands of the isoelectronic SO_3 molecule except that the range of the bands in the case of the metaphosphate is compressed relative to the range of the SO_3 bands. The entire valence-band-envelope for the metaphosphate is also shifted higher into the valence region (to smaller binding energies) relative to the SO_3 envelope, this probably being at least partially due to the negative charge on the metaphosphate. The metaphosphate valence-band range is also compressed relative to the spread of the valence bands of the alkali nitrates, as exemplified in Table VIII (p 46). This is as might be expected on the basis of

comparisons of the nitrate-metaphosphate group spectra with the BX_3-AlX_3-GaX_3-InX_3 (where X = F, Cl, Br, I) group spectra.[50] The valence spectral bands of the boron aluminum, gallium, and indium trihalides have been discussed and compared in detail by Berkowitz.[39] In each case there is a sharp contraction of the valence-band range on going from BX_3 to AlX_3, with a much smaller decrease in range on going from AlX_3 to GaX_3 to InX_3. The spectral band values for $AlCl_3$ are given in Table VIII (p 46) for comparison with the unadjusted values for BCl_3. Based on these comparisons the PO_3^- spectrum should closely resemble the spectrum of NO_3^- except for the contraction of the spectral range. This is what is observed. The onsets of the first bands for $NaPO_3$ and $CsPO_3$ are at approximately 9.0 and 8.7 eV respectively. These values agree well with the mass spectrometric appearance potentials as reported by Steblevskii et al.,[49] especially since the electron-impact values they give are expected to be slightly higher.[8]

The bands have also been assigned on the basis of theoretical calculations related to a D_{3h} PO_3^- only minimally perturbed by the alkali metal cation. The effect of the alkali metal cation on the PO_3^- anion would be to shift the orbital energies deeper by several eV. The data in Table VII (p 45) for PO_3^- have been adjusted by Q-factors to bring them in line with the experimental results, and in the ab initio instances the necessary values are several eV deeper. The outer valence MOs ($1a_2'$, 1e", and 4e') are largely O2p in character, the $1a_2'$ and 1e" being entirely non-bonding and the 4e' being slightly P-O bonding due to a small P3p contribution to the MO. The 3e' and $1a_2"$ MOs are principally P-O bonding orbitals with a significant P3p contribution. An

additional band is observed in the spectrum of $CsPO_3$. It is assignable to ionizations from the 5p levels of Cs^+. This is analogous to the assignments by Potts and Williams[40] for the gaseous cesium halides (Figure 9, p 33), to the assignments by Vick et al.[14] for gaseous $CsReO_4$ (Figure 10, p 34), and to the assignments for $CsNO_3$ (see Chapter II). The spin-orbit split of the Cs 5p level was observed for $CsReO_4$,[14] for $CsNO_3$, and for CsCℓ, CsBr, and CsI[40] but is not observed for $CsPO_3$. It is not known whether both bands are under the observed envelope or if the second band which should be of lower intensity and at a higher ionization energy than the first band was never seen above the background. The second seems the more reasonable possibility especially since the band is expected to be seen in a region approaching the upper energy limit of the He(I) spectrometer.

CHAPTER IV

SOME ALKALI CYANIDES

A. Abstract

The high-temperature He(I) photoelectron spectra of gaseous NaCN and KCN have been obtained using a modified cylindrical-mirror analyzer. The vapors were produced with an internally-located resistance-heated sample oven. The identities of the vapor species were ascertained on the basis of mass spectrometric data, both vapor and matrix-isolation infrared spectroscopic data, and microwave spectroscopic data. The spectral bands are assigned molecular orbital origins through the use of molecular orbital calculations, comparisons with X-ray, He(I), and He(II) photoelectron data on the solids, and analogies to other compounds of similar electronic structure.

B. Introduction

A good deal of data have been collected on the gaseous alkali cyanides including mass spectrometric, microwave, and infrared investigations. In addition, a sizeable number of theoretical calculations have been carried out on these compounds and on the cyanide anion. Since mass spectrometric analyses of the vapors over several of the heated alkali cyanides indicate that they volatilize to stable vapor species, the present photoelectron study of these molecules was undertaken.

C. Experimental Procedure

All spectral measurements were made using a modified truncated cylindrical-mirror analyzer which has been described previously.[11] The spectrometer was equipped with an internally-located resistance-heated tantalum-strip-wound quartz cell for the volatilization of the alkali cyanides. The cell was coated with a high-temperature ceramic cement and was heated by a 0-12 volt AC power supply. The procedures for sample handling and spectral accumulation have also been described previously[13] and will not be repeated here. The cyanides of Na, K, and Rb were obtained commercially. Except for drying, they were used as obtained.

D. Results

The He(I) photoelectron spectra of the vapors above heated NaCN are presented as Figure 15 (p 52) and Figure 16 (p 53). Figure 15 (p 52) represents the spectrum of the vapors at a temperature in the region of initial volatilization and Figure 16 (p 53) represents the spectrum of the vapors at a more elevated temperature. The He(I) photoelectron spectrum of the vapors above KCN is presented as Figure 17 (p 54). Each is a typical spectrum chosen from 20 or more spectra obtained for each case. The spectral peaks for each compound, NaCN at higher temperatures and KCN, are labeled with the average experimental ionization energy values (rounded to one decimal). Unnumbered peaks which are designated by the letters Ar and W are due to argon and water, respectively, which were used as calibrants. Ionization energy values for NaCN and KCN are listed in the first two rows of Table IX (p 55).

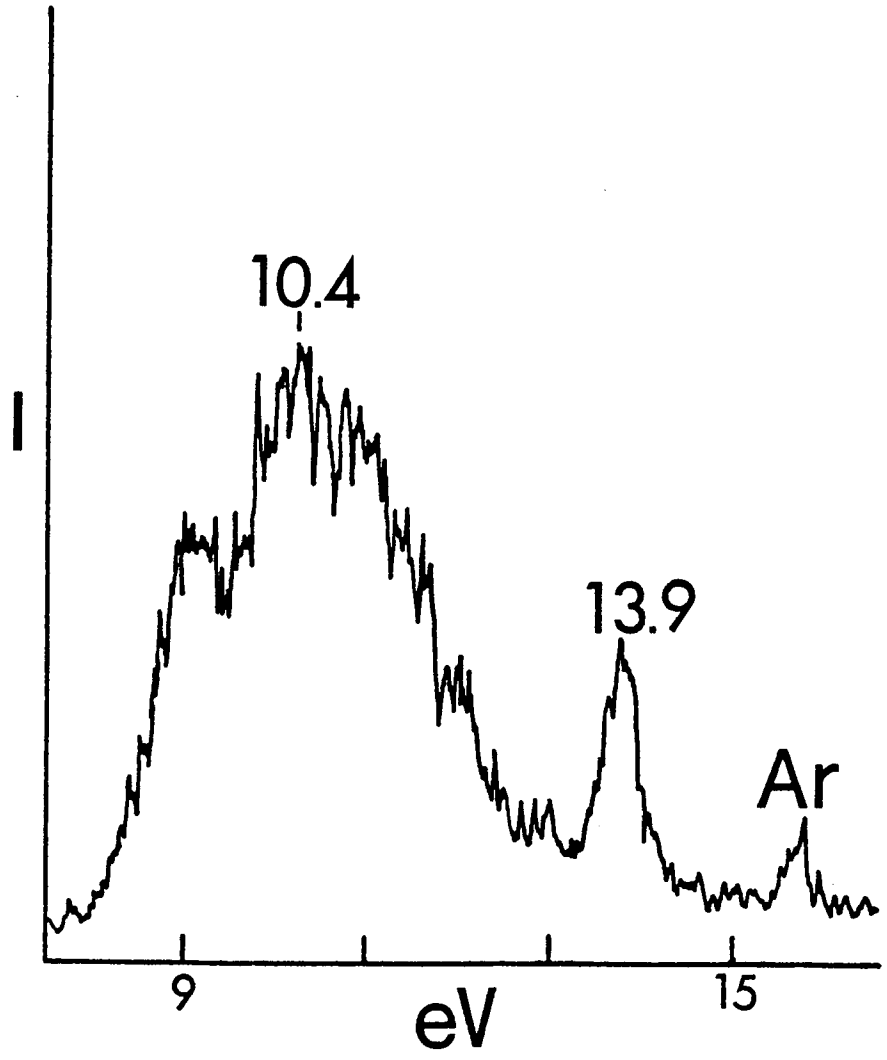

Figure 15. He(I) photoelectron spectrum of NaCN vapor in the temperature region of initial volatilization.

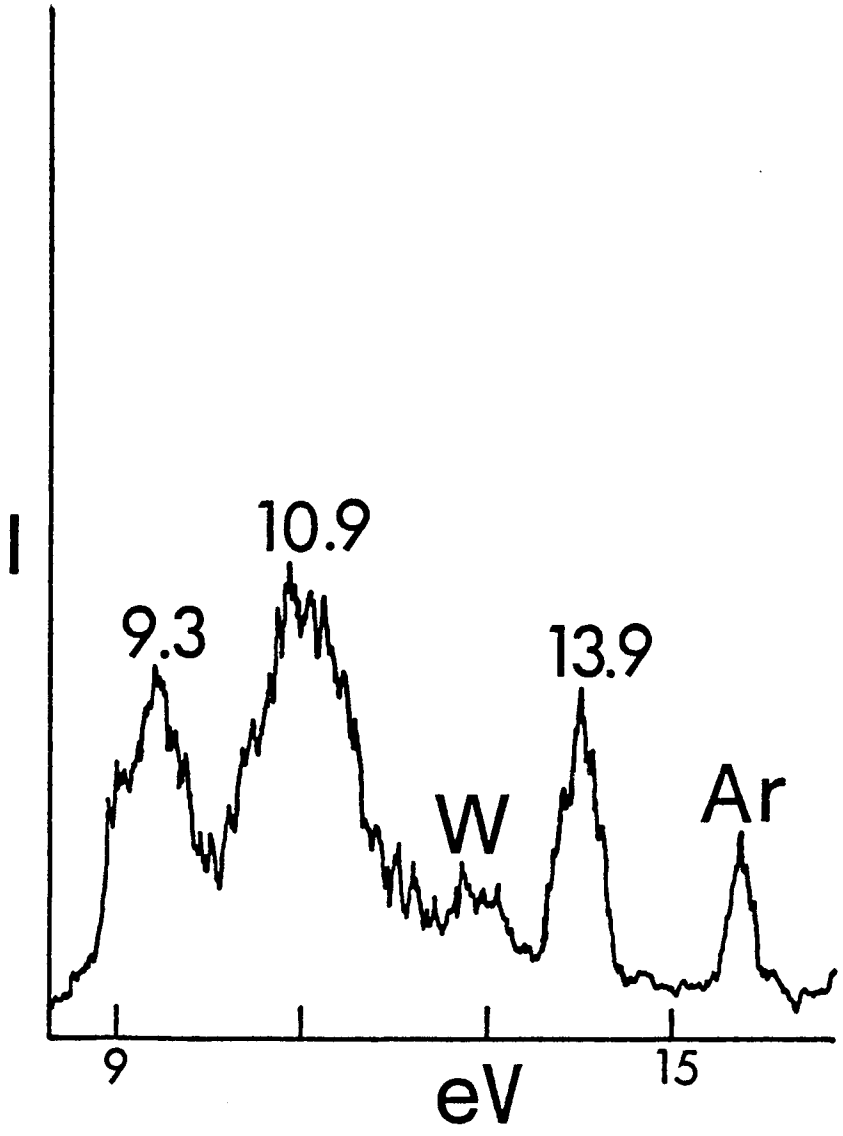

Figure 16. He(I) photoelectron spectrum of NaCN vapor at an elevated temperature.

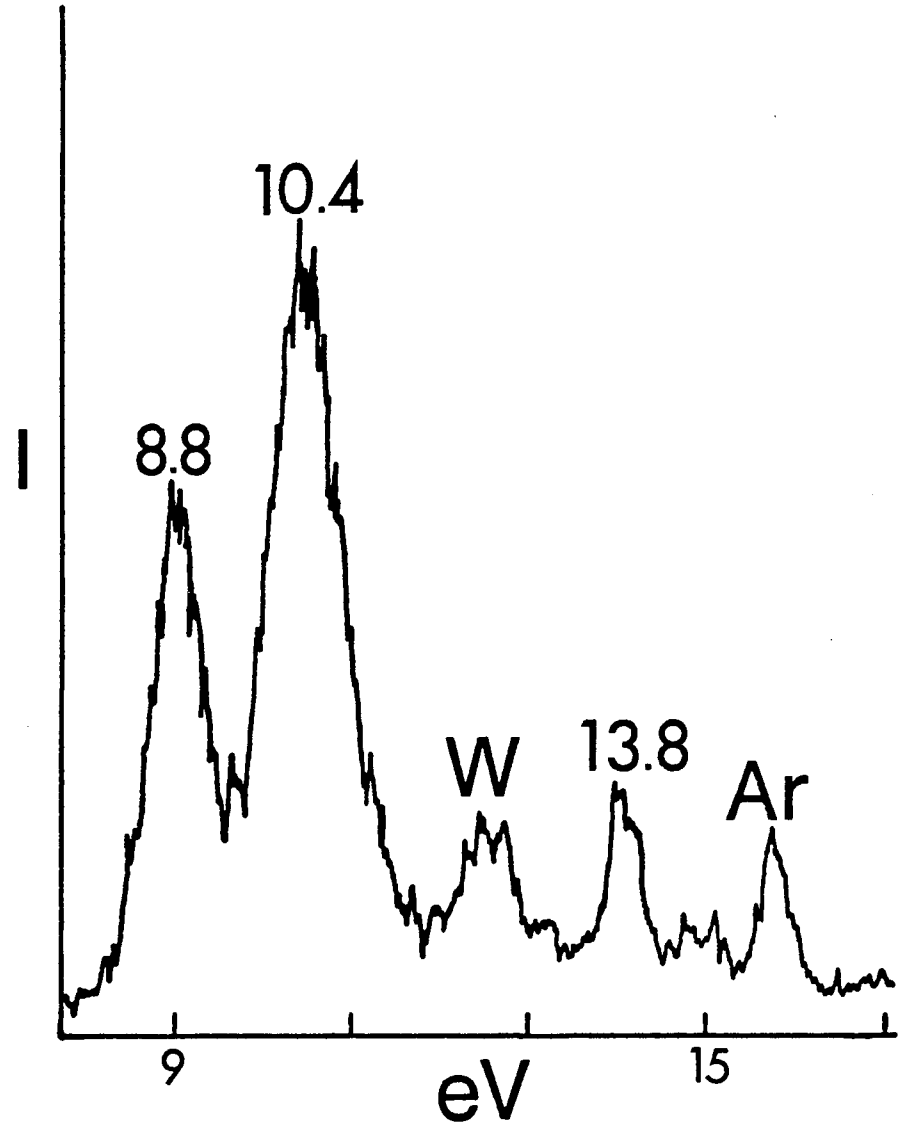

Figure 17. He(I) photoelectron spectrum of KCN vapor.

TABLE IX

CYANIDE EXPERIMENTAL VALUES (-eV)

Procedure	3σ	1π	2σ
He(I) PES on vapor NaCN	9.25[h]	10.87[h]	13.94[h]
He(I) PES on vapor KCN	8.81[h]	10.35[h]	13.83[h]
XPES on solid NaCN[a] (-3.3 eV)	9.3	9.3	12.3
XPES on solid NaCN[b] (-4.0 eV)	9.3	9.3	13.0
XPES on solid KCN[c] (-3.6 eV)	8.8	8.8	12.5
XPES on solid NaCN[d] (+0.9 eV)	9.3	9.3	13.0
XPES on solid NaCN[e] (-4.3 eV)	9.3	10.2	13.2
XPES on solid KCN[e] (-3.2 eV)	8.8	8.8	11.2
He(I) PES on solid NaCN[f] (+0.9 eV)	9.3	10.6	12.8
He(II) PES on solid NaCN[f] (+0.9 eV)	9.3	10.6	12.8
He(I) PES on gaseous CO[g] (+4.7 eV)	9.3	12.2	14.8
He(I) PES on gaseous N_2[g] (+6.3 eV)	9.3	10.7	12.5

[a] Ref. 61.

[b] Ref. 56.

[c] Ref. 63.

[d] Ref. 64.

[e] Ref. 62.

[f] Ref. 58.

[g] Ref. 67.

[h] ± 0.04 (95 percent confidence limits).

These values are the unweighted averages of the values taken from all spectra obtained and are followed by the characterizing 95 percent confidence limits.

A sample alleged to be RbCN was obtained commercially and a spectrum was obtained of the vapors above the heated solid. The obtained spectrum was quite reproducible; however, it was not consistent with the high-temperature spectra obtained for NaCN and KCN, thus leading to the conclusion that the sample was probably grossly impure or did not contain RbCN at all.

E. Interpretive Tools

The high-temperature stabilities and volatilities of several of the alkali cyanides have been determined by mass spectrometric investigations. A preliminary mass spectrometric analysis of the vapors over heated LiCN indicated that the vapor is composed of monomer, dimer, and trimer.[51] Porter[52] observed the mass spectrum of the vapors over NaCN in the temperature region 903-1049°K. He discovered that both monomer and dimer are present with the dimer predominating. More recently, a mass spectrometric study has shown that KCN sublimes and vaporizes in the region of 700 to 1405°K without decomposition to predominantly dimer, substantial amounts of monomer, and small amounts of trimer.[53] Appearance potentials for the KCN^+ and K_2CN^+ ions were determined to be approximately 9.3 and 10.3 eV, respectively.[53]

Several infrared studies, utilizing both vapor and matrix-isolation techniques, have also been carried out on several of the alkali cyanides. Ismail, Hauge, and Margrave[51] have trapped the vapors above

heated LiCN in Ar, Ne, and N_2 matrices and have measured the infrared absorption frequencies. Three bands were assigned to the monomer and other bands assignable to polymers were noted but were not treated in detail. The infrared absorption spectra of NaCN and KCN vapors at temperatures of 1073 to 1273°K have been recorded by Leroi and Klemperer.[54] Bands assignable to both monomer and dimer species were observed. The vapors above heated NaCN and KCN have also been isolated in inert gas and N_2 matrices.[55] In each case, several bands were assigned to a linear monomer, four bands were assigned to a cyclical Na-CN-Na-CN dimer (rhomboidal D_{2h}), and three other values were assigned to other polymers. In the case of the monomer lines isotopic frequency shifts provided further substantiation of the assignments.

Table X (p 58) is a compilation of theoretical calculations for the CN^- ion and some alkali cyanides. Bak, Clementi, and Kortzeborn[59] have conducted ab initio Hartree-Fock calculations for LiNC and LiCN. They reported a marginal energy difference of 0.38 eV in favor of LiNC. Clementi, Kistenmacher, and Popkie[65] have followed this calculation by further computations in which they mapped the energy surfaces for various positions of the Li^+ around the CN^-. They found that the lowest energy path leading from LiNC to LiCN will permit the Li^+ to "orbit" the CN^- upon excitation of about 0.3-0.4 eV. Such a situation is one for which no traditional preferred structural formula can be drawn. The Li-N-C bending vibrations corresponding to high quantum numbers may thus bring about an orbiting of the Li^+ about the CN^-. The writers stated that this interesting type of bond may turn out to be somewhat common for high-temperature species in which thermal excitation is sufficient

TABLE X

CYANIDE THEORETICAL CALCULATIONS (-eV)

Procedure	3σ	1π	2σ
Ab initio on CN^{-} [a]	9.3	9.7	13.2
Iterative Extended Hückel on CN^{-} [b]	9.3	11.0	14.0
STO-3G on CN^{-} [c]	9.3	10.7	14.2
Ab initio on CN^{-} [d]	9.3	9.7	13.2
SCF on CN^{-} [e]	9.3	9.4	13.35
Extended Hückel [f]	9.3	9.9	15.4
Ab initio on $Li^{+}NC^{-}$ [g]	9.3	10.1	14.5
STO-3G on $Na^{+}CN^{-}$ [h]	9.3	9.3	13.4

[a] Ref. 56, adjusted by Q = -4.9 eV.

[b] Ref. 56, adjusted by Q = +1.8 eV.

[c] Ref. 57, adjusted by Q = -10.5 eV.

[d] Ref. 58, adjusted by Q = -4.6 eV.

[e] Ref. 60, adjusted by Q = -4.1 eV.

[f] This paper, adjusted by Q = -0.5 eV.

[g] Ref. 59, adjusted by Q = +1.5 eV.

[h] Ref. 57, adjusted by Q = -2.7 eV.

to produce the requisite vibrational excitations. They refer to the bond as a polytopic bond. Rambidi[29] has employed a relatively simple electrostatic model for LiNC and has arrived at comparable results. His model indicates that the interaction energy varies only slightly for the movement of the cation on an approximately oblate surface circumscribed around the anion. That is, only small variations in interaction energy are encountered upon large displacements of the Li^+ relative to the CN^-.

More recently Kuijpers, Törring, and Dymanus[66] have obtained the microwave spectrum of the vapors over heated KCN in the region of 873°K. Their tentative conclusion was that the basic structure of the potassium cyanide gaseous monomer is a diatom in which the CN^- group behaves as one atom (pseudo-halogen). The rotational-vibration spectrum of such a diatom is heavily perturbed by the free or unhindered rotation of the CN^- group and the large number of lines found may be ascribed to vibrational effects and splittings because of the motion of the CN^- group. This is quite similar to the theoretically-based conclusions discussed above pertaining to polytopic bonding.

In addition, theoretical extended Hückel calculations have been carried out for the potassium cyanide dimer. The calculated values have been adjusted by a Q-factor of -3.2 eV to bring them in line with the mass spectrometrically-determined appearance potential of the K_2CN^+ ion of approximately 10.3 eV.[53] The orbital energies and assignments are as follows: 10.3 (b_{1u}), 13.9 (a_g), 14.2 (b_{3g}), 14.3 (b_{2g}), 14.5 (b_{2u}), 14.7 (b_{3u}), 16.7 (b_{1u}), 18.5 (a_g).

F. Conclusions

Data pertinent to the interpretation of the NaCN and KCN vapor spectra are presented in Table IX (p 55) and Table X (p 58). All values, both experimental and theoretical, have been adjusted to the first peak value in the NaCN or the KCN vapor spectrum and rounded off to the nearest 0.1 eV. In addition, for comparison, the He(I) and He(II) photoelectron spectra of solid NaCN are presented in Figure 18 (p 61) and the He(I) spectra of CO and N_2 (isoelectronic with CN^-) are presented as Figure 19 (p 62) and Figure 20 (p 63). The assignment of molecular orbital origins for the three peaks in both the NaCN and KCN monomers (Figures 16 and 17, pp 53 and 54, respectively) are made on the basis of a CN^- anion with minimal perturbation by the associated cation. In each case the MO assignments are concluded to be 3σ, 1π, 2σ. This is supported by the similarities of the band shapes obtained in this work with those reported for the He(I) spectrum for solid NaCN (Figure 18, p 61).[58]

In 1972, Morrison and Hendrickson[56] observed the X-ray PES spectrum of solid NaCN and assigned bands at 5.3, 9.0, and 12.8 eV to the 3σ, 1π, and 2σ molecular orbitals, respectively. Later X-ray PES studies of solid NaCN and KCN by Vannerberg,[62] of solid KCN by Calabrese and Hayes,[63] and of solid NaCN by Nefedov et al.[64] have shown that Morrison and Hendrickson's assignments are quite questionable. The most convincing evidence is the X-ray band intensity calculations by Calabrese and Hayes.[63] These computations showed that the 1π MO band should be considerably less intense than the 3σ or 2σ when using an X-ray source (a $3\sigma:1\pi:2\sigma$ intensity ratio of 7:2:8 was obtained). For solid NaCN,

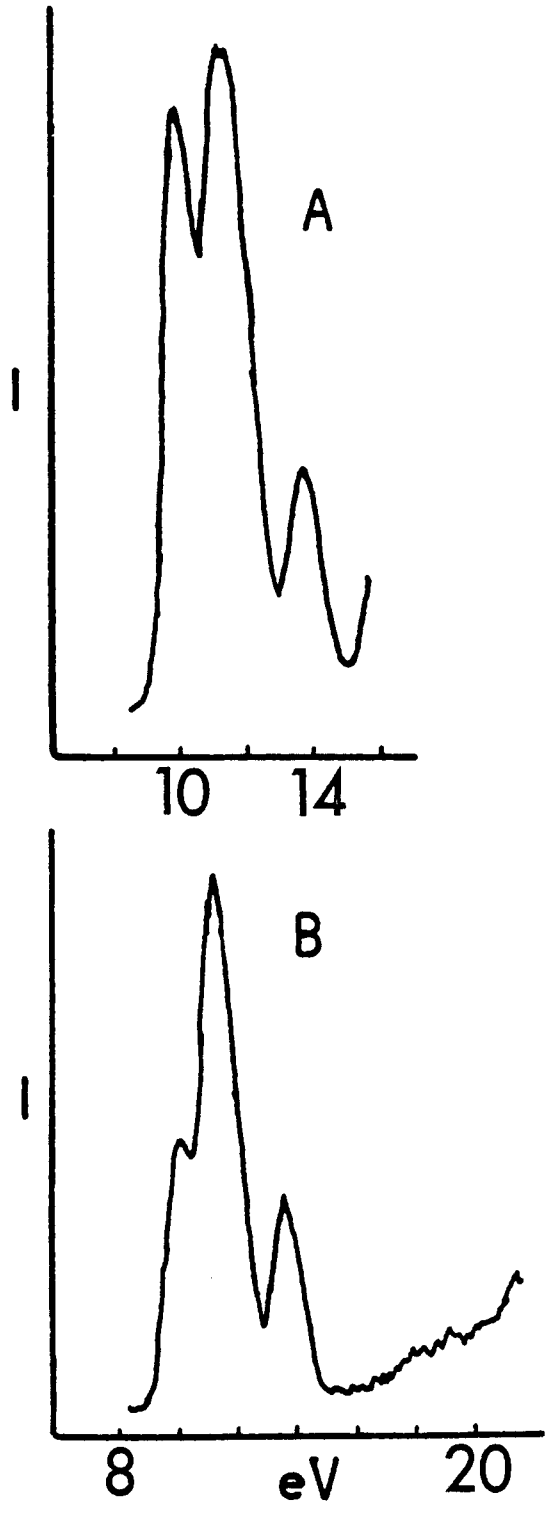

Figure 18. Photoelectron spectra of solid NaCN, (A) He(I), (B) He(II).

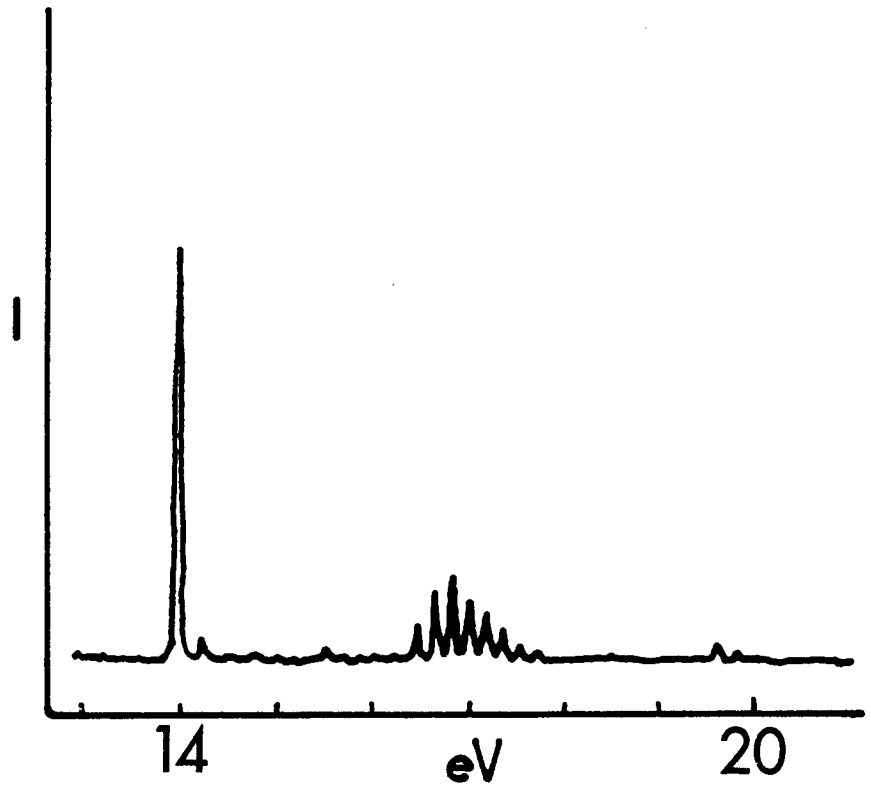

Figure 19. He(I) photoelectron spectrum of CO.

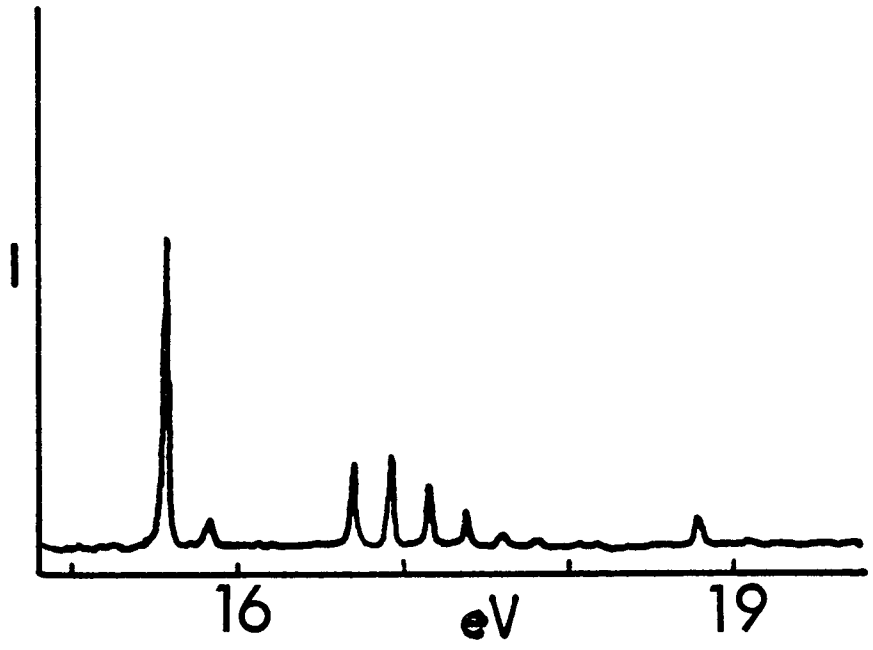

Figure 20. He(I) photoelectron spectrum of N_2.

Vannerberg[62] observed X-ray PES bands at 5.0, 5.9, and 8.9 eV with relative intensities of 6:3:8 which he assigned to the 3σ, 1π, and 2σ MOs on the basis of the theoretical calculation of Clementi and Klint[60] and the intensity calculations of Calabrese and Hayes.[63] He also observed a rather weak band at 11.5 eV which he attributed to shake-up. Nefedov et al.[64] made similar assignments for their X-ray PES spectrum of solid NaCN. More recently Considine, Connor, and Hillier[58] also called Morrison and Hendrickson's assignments into question on the basis of their own calculations of X-ray cross sections. (Relative values of 1.0 (3σ), 0.6 (1π), and 4.5 (2σ) were obtained.) They also obtained the He(I) and He(II) photoelectron spectra of solid NaCN. In each case they obtained three clearly separated bands at 10.2, 11.5, and 13.7 eV which they attributed to the 3σ, 1π, and 2σ MOs, respectively. They based these assignments on ab initio calculations for the CN^- ion and more importantly upon their calculated photoionization cross sections for both He(I) and He(II) ionization sources. The enhanced intensity of the 1π MO in the He(I) and He(II) PES was very helpful in making assignments for the bands. These cross section considerations, showing the relative He(I) cross sections to be 0.3 (3σ), 1.0 (1π), and 0.5 (2σ), also support the assignments made in this paper.

Correlation of all the spectral bands to the monomer might seem inconsistent with the results of the mass spectrometric studies for NaCN and KCN which show the dimer to be the predominant vapor species with significant or almost equal amounts of monomer. It must be remembered, though, that the mass spectral results are for equilibrium situations. Conditions in the present experiments, however, are nonequilibrium ones.

It has been observed in several previous instances that polymerization has been notably diminished in other vapors of ionic compounds containing complex anions. Another consideration is that the dimer molecular orbitals would have lower cross sections relative to those of the monomer orbitals because the number of valence orbitals is double that of the monomer. This would effectively decrease the possibility of observing dimer-associated bands above the background. On this basis, Figure 15 (p 52) is believed to be the spectrum of a mixture of sodium cyanide monomers and dimers at the lower volatilization temperature. When the temperature is increased the spectrum approaches that depicted in Figure 16 (p 53), which is believed to be the monomer NaCN spectrum. This is as should be expected on the basis of thermodynamic equilibrium considerations. As the temperature is raised the dimer-monomer equilibrium should be shifted toward the monomer. The elevated-temperature NaCN spectrum (Figure 16, p 53) is thus believed to be the situation in which the monomer is the predominant vapor species but there probably is still some dimer.

CHAPTER V

CONCLUSIONS

A. Review of Conclusions

The experimental photoelectron spectral bands and ionization energies for some alkali nitrates, metaphosphates, and cyanides have been assigned molecular orbital origins and correlated with theoretical MO calculations for the neutral monomeric molecular species and for the free anions. In each case, mass spectrometric results and previous volatilization observations were used to make vapor composition judgments. (The vapors above the heated solids KNO_3, $RbNO_3$, $CsNO_3$, $NaPO_3$, KPO_3, $RbPO_3$, $CsPO_3$, NaCN, and KCN were all concluded to be composed predominantly of the corresponding gaseous monomers.) To assist in molecular orbital assignments, the spectra were compared with X-ray, He(I), and He(II) photoelectron energies and intensities of the corresponding solids, and were compared with photoelectron data for isoelectronic and valence isoelectronic species.

In the cases of the nitrates, metaphosphates, and cyanides for which reproducible spectra could be obtained, band assignments were made principally on the basis of calculated electronic structures for the corresponding anions minimally perturbed by the associated cation. In practice, these correlations were carried out by application of Q-factors to the theoretically computed data for the free anions. The PES spectra of all species containing the same anion with different alkali cations were very similar. These observations led to the possibility that a

newly-proposed high-temperature structural model called polytopicity might be applicable to these vapor molecues. Observations of the same kind were noted in two previous high-temperature PES studies on similar complex-anion compounds,[13,14] but these data could not be used to arrive at any conclusions pertaining to the possible polytopicity of the molecules studied. Likewise, after consideration of polytopic bonding and the present photoelectron studies in relation to this model, it was found that no judgment could be made concerning the possible polytopicity of these species. In the next section polytopic bonding will be described in more detail and reasons for the conclusion concerning it will be presented.

B. Polytopic Bonding

Several investigators in recent years have proposed the idea of polytopic bonding to describe a number of monomeric gaseous ionic compounds made up of a simple cation and a complex anion.[29] Such vapors might include MOH, MCN, MNO_3, M_2SO_4, M_2WO_4, M_2MoO_4, $MReO_4$, $MA\ell F_4$, and MBO_2 where M is an alkali metal or univalent thallium. The idea of polytopicity was prompted by theoretical calculations and by observations which have been noted in electron diffraction, infrared spectral, and microwave studies. The data in many cases point to the possibility that classical fixed-nuclei models for these vapor monomers at high temperatures are not entirely adequate, and that a model in which the cation makes large-amplitude motions with respect to the complex anion might fit better. Alternately, a model in which the cation relates equally to all of the ligands of the complex anion may be employed.

Experimental electron diffraction data (on MBO_2, MNO_3, $MReO_4$, M_2SO_4, Na_2CrO_4, Cs_2MoO_4, Cs_2WO_4, $NaA\ell F_4$, $KA\ell C\ell_4$, $T\ell InC\ell_4$) have been interpreted to indicate that the complex anion shows high symmetry with all bond angles and bond distances being essentially equal, and that the geometry of the complex anion is not greatly altered by the cation.[68] The root-mean-square amplitudes of the vibrations involving the cation are extraordinarily high, 0.20Å and above, as compared to those only involving the anion atoms, in the range 0.03-0.07Å; and the lengths of the bonds involving the cations are unusually long as compared to such bonds in simple compounds. As the vapor temperature is increased, less usable structural information can be obtained from the diffraction patterns, especially information regarding the cation, and in a number of cases features characteristic of an associated cation seem to be missing.

These observations have been taken to indicate that the high-temperature vapors consist of a relatively rigid and symmetrical complex anion only moderately perturbed by the cation which shows considerable freedom of motion relative to the anion. This freedom of motion is assignable to population of higher vibrational levels of the molecules, the levels being those associated with the weakly-bonded cation and thus being those requiring small amounts of excitation energy. It has been proposed that the cation motions might be represented as large displacements occurring on the surface of an imaginary sphere (or other appropriate surface of high symmetry) circumscribed about the complex anion. With sufficient excitation, the molecule could be viewed as having a dynamic configuration in which the cation is seen as belonging to all anion ligands with equal probability.

Several of these gaseous complex anion compounds have also been studied by infrared spectroscopy (MOH, NaCN, KCN, MBO_2, $CsNO_2$, $CsNO_3$, $MReO_4$, $LiAlF_4$, $NaAlF_4$).[69] Some usable data have been obtained, even though the investigations have been beset by numerous experimental difficulties largely due to thermal excitation. It has been observed that the vibrational frequencies of the complex anion are independent of the cation or nearly independent of the cation in the vapor species, and that the cation-involved frequencies (especially the bending frequencies) tend to be quite low (ca 120 cm^{-1} and below) and in some cases spectral lines associated with these frequencies seem to be missing. Several of the investigators have interpreted these observations to indicate that no single, simple description of the cation-to-anion bonding in these compounds is completely satisfactory. They imply that a dynamic model might work better to explain the data. This approach fits well with the views expressed by the electron diffraction workers. In addition, infrared investigations have been carried out on matrix-isolated vapors (MOH, MCN, MBO_2, MNO_3, $MClO_3$, $MClO_4$, K_2SO_4, Rb_2SO_4, $MAlF_4$).[70] These studies show that the cation-involved frequencies are quite low, an observation in accord with the vapor infrared studies.

The only gaseous compound of this type which has been investigated by microwave spectroscopy is KCN.[71] Because the compound is a ternary one and the temperature required for volatilization is relatively high, the spectrum tends to be so complicated that interpretation is difficult. This complication may be assignable to population of numerous excited rotational and vibrational levels which results in a large number of lines and a consequent reduction of individual line intensities. The

overall behavior seems compatible with the idea of polytopicity, as the author notes. Similarly, little work has been done on these compounds with vapor Raman spectroscopy. The available spectra (on $InAlF_4$ and $InAlCl_4$)[72] do not show sufficient resolution to permit a decision regarding the symmetry of the complex anion. There is a possibility that results may be more conclusive with this method and other investigations are now being attempted.

In addition to these experimental observations a number of relevant theoretical calculations have been carried out. Initially, Bak, Clementi, and Kortzeborn[59] produced a detailed set of quantum-mechanical calculations which showed that only a marginal energy difference of about 0.4 eV exists between LiNC and LiCN. Clementi, Kistenmacher, and Popkie[65] followed this by mapping the energy surface for various positions of the Li^+ ion around the CN^- anion. They found that the lowest energy path from Li-NC to Li-CN will permit the Li^+ to "orbit" the CN^- upon excitation of about 0.3-0.4 eV. They stated that the situation is one for which no traditional preferred structural formula can be written. Other ways of interpreting their conclusions are to say that the Li-N-C bending vibrations change, in the limit, to an orbiting of the Li^+ around the CN^-, or to say that the Li^+ has an equal probability of being at any position on the energy surface about the CN^-.

Rambidi[29,73] followed these calculations with computations on LiNC assuming a relatively simple electrostatic model. He arrived at results very similar to those of Clementi et al.[65] Going on to treat $CsNO_3$, $TlReO_4$, and $NaAlF_4$ by the same model, he found that in each case there was a wide range of computational parameters for which the

interaction energy varied only slightly for motion of the cation on an approximately spherical surface (or other appropriate surface of high symmetry) circumscribed about the complex anion. That is, only small variations in interaction energy result from large displacements of the cation relative to the anion.

Dementjev and Kracht[74] conducted a quantum-mechanical ab initio analysis of the $LiBO_2$ vapor monomer. The results are quite similar to those for LiNC, with large amplitudes of vibration of the Li^+ and a small force constant for this vibration. The investigators therefore believe that the molecule should be considered to be polytopic. Rambidi[75] had previously made calculations of the root-mean-square vibrational amplitudes of the MBO_2 monomer (with M = Li, Na, and Rb) for various temperatures. Comparisons of values for various atom pairs at 0°K and 1500°K are quite interesting. For example, the root-mean-square amplitude of the Na-O (stretching vibration) is 0.057Å at 0°K and 0.129Å at 1500°K while for the B=O (stretching vibration) the values are 0.035Å at 0°K and 0.042Å at 1500°K. The 1500°/0° ratio is 2.26 for Na-O as compared to only 1.20 for B=O. Similar values were obtained for $LiBO_2$ and $RbBO_2$ as well as for other pertinent compounds such as MCN, MNO_3, $MCℓO_3$, and M_2SO_4. The results of such computations can be taken as an indication that these compounds constitute dynamic systems in which the alkali metal cations which are weakly bonded to a relatively rigid complex anion exhibit large displacements due to excitations involving low-frequency M-O or (M-appropriate ligand) vibrations.

Other views have also been expressed in explanation of these findings. One investigator[76] has suggested quantum-mechanical tunneling

with penetration of the walls of the energy wells. Still another way of interpretating the nonrigidity, as stated previously, has been to assume that the cation belongs to all anion ligands with equal probability. However, in any case, the excitation energy required for mobilizing the cation is largely supplied by the thermal energy employed to volatilize the compound.

In an effort to ascertain whether the technique of PES might be applicable to decisions on the geometries of ternary compound vapor monomers, a series of theoretical calculations have been made. Selected results were shown in Table IV (p 25) and described in Chapter II. Using semi-empirical procedures, molecular orbital energy calculations have been conducted for $K^+NO_3^-$ in C_S, C_{2V}, and C_{3V} configurations and for the D_{3h} NO_3^- ion. As the symmetry is reduced from D_{3h} to C_{3V} to C_{2V} to C_S splits in the bands have been followed. In almost all instances the splitting is of the order of 0.1-0.2 eV. When one observes the band breadths in the experimental spectra, they are usually considerably more than 0.2 eV. Indications are, therefore, that PES investigations using presently available techniques will probably not be able to permit one to select among the various geometric possibilities. Further, it is not now possible to be sure, but indications are that higher resolution experiments might not be of any more assistance. It is difficult to tell the difference between band broadening produced by perturbation of the symmetry of the initial molecule and band broadening produced by the Jahn-Teller effect upon photoionization. That is, the band broadening produced by the effect of a localized Cs^+ upon a D_{3h} NO_3^- (reducing the symmetry from D_{3h} to C_{2V}) is difficult to distinguish from the band

broadening produced by the Jahn-Teller effect upon ionization of a minimally perturbed or isotropically perturbed D_{3h} NO_3^-.

C. Conclusion

The photoelectron spectroscopic investigation of vapors produced by heating inorganic ionic solids has advanced rapidly during the past few years and has been extended to a wide variety of compounds. The major results have been the measurement of the ionization energies which may be correlated to MO structures of the neutral vapor molecules. In the present study, it has been shown that the photoelectron spectra of the vapors above heated KNO_3, $RbNO_3$, $CsNO_3$, $NaPO_3$, KPO_3, $RbPO_3$, $CsPO_3$, NaCN, and KCN are assignable to the corresponding molecular vapor monomer, and the bands may be assigned MO origins on the basis of theoretical MO calculation for the free corresponding anion. Although no high-temperature structural conclusions could be made on the basis of this study, it is hoped that this work may provide insight into further investigations of high-temperature vapors and the structural models which might be applicable to them.

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LIST OF REFERENCES

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