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ELECTRONIC MATRIX ISOLATION SPECTROSCOPIC STUDIES OF METAL ATOM PHOTOCHEMISTRY

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ELECTRONIC MATRIX ISOLATION SPECTROSCOPIC STUDIES
OF METAL ATOM PHOTOCHEMISTRY

By

MONTE ALLAN DOUGLAS

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

DOCTOR OF PHILOSOPHY

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HOUSTON, TEXAS

APRIL, 1982
ABSTRACT

ELECTRONIC MATRIX ISOLATION SPECTROSCOPIC STUDIES

OF METAL ATOM PHOTOCHEMISTRY

By

MONTE A. DOUGLAS

This dissertation presents the results of chemical research efforts directed in three areas: (1) the final design of an ultraviolet-visible absorption and emission matrix isolation apparatus is described, (2) by employing this apparatus, molecular scale interactions of the 1:1 metal-water adduct are investigated utilizing electronic absorption spectroscopy, and (3) molecular orbital and electronic state-to-state correlations are invoked to interpret the chemical reaction dynamics of the adducts along ground and excited potential energy surfaces. The final design of this matrix isolation apparatus incorporated unique features that abbreviated data acquisition time and obviated several experimental problems that have plagued previous matrix isolation studies.

The investigations of the molecular interactions and reactions of the Group IIA metal atoms (Mg, Ca, Sr, Ba), the Group IIIA metal atoms (Al, Ga, In), and the Group IVA metal atoms (Si, Ge, Sn, Pb) with water molecules isolated
in rare gas matrices at 15 K are reported. In most instances, the strength of the metal-water interaction is sufficiently strong to perturb significantly the electronic structure of the metal atom which results in a unique band structure for the adduct that is red-shifted from the metal atomic resonance transition. Selective photolysis studies contributed to a better understanding of the electronic structure of the adduct. Molecular orbital theory is invoked to interpret the nature of the ground and excited states of the metal-water adduct.

By resorting to molecular orbital and electronic state correlation methods, the qualitative features of the metal-water interaction potential energy surfaces are derived which predicate the chemical reaction dynamics that, in turn, result in a fundamental understanding of relative reactivities, photochemical pathways, and chemiluminescent processes.

In addition, this dissertation reports studies of the electronic structures of the Group IIIA metal suboxides (Al₂O, Ga₂O, In₂O) in absorption and emission. Progressions in the symmetric stretching and bending modes for the ground and excited states are observed.

Finally, previously undocumented electronic structures of several metal dimers (Al₂, Ba₂, Ge₂) are reported and discussed.
TO MY FATHER AND MOTHER:
ROBERT AND JEAN DOUGLAS
ACKNOWLEDGMENTS

It is with great pleasure that I express my gratitude for the contributions my father and mother have made to my education. Their gracious extensions of financial assistance for my education and of continuous encouragement in my academic endeavors were invaluable; however, my appreciation for their display of patience and perseverance in instilling the principles of discipline, respect for authority, achievement, and many other establishment concepts in my character is ineffable.

I am indebted to my research advisor, Dr. John L. Margrave, for his warm expressions of confidence, encouragement, and direction during my graduate years. His stature as the gentleman scholar has made an indelible impression on my professional escutcheon.

I would like to thank Rice University and the Robert A. Welch Foundation for providing predoctoral Fellowships.

Additionally, I would like to thank Mrs. Donna Montez for her diligent and thoughtful efforts in preparing the final version of this dissertation.

It is with great honor that I acknowledge the courageous and principled efforts of the professional and citizen soldiers in the military establishment of the United States
of America during her two centuries of existence as a client nation to God. As a consequence of their efforts in times of war and in times of peace, freedom for this country has been won and maintained. Within the framework of this precious and honorable freedom, I have had the tremendous opportunity to pursue my academic goals. No expression of appreciation is too great for the honorable actions of these dutybound men.

Finally, I would like to extend my highest appreciation for the logistical grace provision of my pastor, Col. R.B. Thieme, Jr., whose faithful doctrinal teachings have provided an objective perspective of and a capacity for the difficult challenges which life has to extend.
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CHAPTER ONE

GENERAL INTRODUCTION
CHAPTER ONE

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   E. SUMMARY AND OVERVIEW
I. GENERAL INTRODUCTION

A. OVERVIEW OF THE MATRIX ISOLATION TECHNIQUE

Initially, the motivation behind the development of the matrix isolation technique was to create a means to characterize unstable and otherwise transient chemical species so as to fill in the void of known unstable species left vacant by other approaches to the problem such as flash photolysis or pulse radiolysis. The matrix isolation technique fulfills this initial design since it involves the entrapment of an unstable species in the interstice of a rigid, inert crystal at cryogenic temperatures. This isolation is achieved by cocondensing a reactive species with copious quantities of an inert material on a substrate maintained at cryogenic temperatures thereby stabilizing the reactive species. The challenge to the researcher is the generation of the unstable species which has already been established for many categories of compounds; consequently, the matrix isolation technique can access a wide variety of previously unstudied reactive species. Measurable concentrations of the unstable species are allowed to accrue during trapping so as to allow one to probe at leisure the "transitory" species with a conven-
tional spectroscopic technique as opposed to time-resolved methods. High concentrations of the reactive species may be maintained since the rigid character of the cage hinders interaction with other species of the same or different type within the matrix by precluding long range diffusion. Naturally, the inert character of the cage material is mandatory so as to prevent interaction with the trapped species. The matrix material must also be transparent to that particular region of the electromagnetic spectrum one desires to study the isolated species of interest. The cryogenic working temperature not only insures a rigid cage character but also extends the lifetime of an otherwise transient species in that it reduces the rate of internal conversion that requires an activation energy which would normally be supplied at higher temperatures. Generally, rare gases are used for the matrix medium; however, other species such as nitrogen or methane are also employed. The cold substrate is maintained at a temperature no greater than one-third of the melting point of the matrix material utilized to insure good cage rigidity. This temperature requirement ranges from 80K for neon to 550K for xenon.

The experimental apparatus employed in matrix isolation studies consists of a vacuum chamber, a trapping substrate that is in good thermal contact with a cryostat, a means of producing the trapped species, and some type of spectro-
scopic instrumentation to investigate the isolated species. A vacuum of less than $10^{-5}$ torr must be achieved and maintained to prevent an excess of residual contaminants from condensing on the cold trapping substrate and to avoid heat transfer from the warm laboratory environment to the cold matrix surface via a gas transport thermal contact. The trapping surface must have a high thermal conductivity at cryogenic temperatures, so as to dissipate radiant heat loads, and be transparent to that region of the electromagnetic spectrum where the entrapped species will be studied. The cryostat may be a liquid hydrogen or liquid helium refrigerated cold finger, or it may employ the open-cycle Joule-Thompson or the closed-cycle helium refrigeration techniques. The chemical species to be studied may be deposited for subsequent trapping in the matrix medium by a gas jet inlet, a Knudsen furnace, sputtering, or bombardment. In some experiments, it is necessary to generate the species of interest. The manner of generation falls into two broad categories: (1) generation at ambient or high temperatures in the gas phase, followed by rapid quenching with excess inert gas, and (2), generation in situ, e.g., by photolysis of matrix isolated parent molecules. A description in-detail of the matrix isolation apparatus and a more technical treatment of the subject of matrix isolation may be found in references 16-19.
After its inception, the matrix isolation technique was applied not only to unstable species but also to stable species for several reasons. First, sharper solute absorptions are observed in the matrix since isolation of a monomeric species reduces intermolecular interactions. However, the absorptions are almost always found to be shifted in value because the presence of the isolating cage perturbs the electronic character of the monomeric species. Secondly, the vibrational spectra of trapped species have narrower bands and are much more distinct due to the almost exclusive absence of rotational spectra. This is true since the limited cage size rarely allows any rotation of the entrapped species, and at low temperatures, the population of upper rotational states is reduced. Hence, near-coincident fundamentals and isotopic splittings that overlap in liquid or vapor phase spectra may often be resolved in the inert solid matrix, and obscure band and frequency assignments may be clarified. However, this is at the expense of shifted absorption values and missing rotational spectra the latter of which, in itself, entails the loss of structural information and symmetry designations.

Presently, the three most important spectroscopic techniques utilized to study matrix isolated species are those of infrared, ultraviolet-visible, and electron spin resonance spectroscopy. However, as of late, applications
of laser induced fluorescence, Raman, Mössbauer, NMR, and SIMS spectroscopies have been made in matrix isolation studies and have been found to be quite useful and practical. The sensitivity of these techniques diminishes according to the following sequence: fluorescence, e.s.r. > U.V.-VIS > I.R. > Raman. The e.s.r. technique also excels in that it is highly selective and sensitive to low concentrations of free radicals, whereas infrared spectroscopy requires a comparatively large amount of sample material before a satisfactory spectrum is secured. At the same time, however, fluorescence, e.s.r., and U.V.-VIS spectra are often difficult to interpret without knowledge of the guest species' identity. Infrared spectroscopy excels in this respect since it is quite informative with regard to the identification of the guest species. In essence, matrix isolation spectroscopy may be considered to be at its best when a combination of spectroscopic techniques can be used cooperatively to identify and characterize the matrix isolated species. The work presented in this thesis is a case in point in that most of the systems explored by U.V.-VIS spectroscopy here have been previously studied in the infrared. As a result one can obtain an enhanced understanding of the excited and ground state chemistry as well as an extended characterization of the intermediate and final chemical reaction products gleaned from a mapping of their electronic structures.
B. BRIEF HISTORICAL SKETCH OF THE MATRIX ISOLATION TECHNIQUE

Often not credited, Vegard, in 1924, was the first to recognizably conduct research in the field of matrix isolation spectroscopy. In the cryogenic research laboratory of Onnes in Leiden, Vegard /1/ observed the emission from oxygen and nitrogen atoms generated by electron, proton, and x-ray bombardment of rare gas mixtures of these species frozen at low temperatures, utilizing liquid hydrogen and liquid helium as refrigerants. Due to the limited availability of these refrigerants at that time, further experimentation was not conducted until almost two decades later when, in 1941, G.N. Lewis /2/ studied the phosphorescence of several aromatic molecules isolated in a rigid medium at low temperatures. The modern inception of the matrix isolation technique, which has since gained contemporary momentum, is credited to Pimentel /3/ who, in 1954, studied the infrared spectra of several small molecules by isolating them in matrices of rare gas solids at cryogenic temperatures. Simultaneously, G. Porter /4/ used argon and nitrogen matrices to study stable and reactive species. In the next few years, however, it was left to Pimentel and coworkers to develop the technique as a viable asset to the research chemist.

Since 1954, many advances in chemical research have been made utilizing the matrix isolation technique, employ-
ing the whole gamut of spectroscopic disciplines. In 1960, Pimentel observed the first infrared spectrum of a free radical (HCO) /5/. In 1961, at the suggestion of Pimentel, Linevsky /6/ studied high temperature species by condensing (LiF)\(_n\) (n=1,2,3), effusing from a Knudsen cell as a molecular beam, with a rare gas on a cold surface. Exploiting this technique as a synthetic method were Margrave /7/, studying gaseous SiF\(_2\), Timms /8/, and others. Andrews and Pimentel /9/, in 1961, developed the alkali metal atom technique which made the stabilization and subsequent characterization of many free radicals and ionic species in the matrix possible. In the mid-1960's, liquid helium refrigerant became much more economical, and later, as a spinoff of the U.S. space program technology, closed-cycle refrigerant systems were made available to the research scientist. The result of these two events was a renaissance of interest in the matrix isolation technique as the financial barriers collapsed. In this new expansion, many new spectroscopic techniques have been employed to study matrix isolated species. In 1971, Claassen /10/ applied Raman spectroscopy to the matrix isolation technique studying the SF\(_6\) spectrum in argon at 4\(^\circ\)K. More recently, Bos /11/ has utilized Mössbauer spectroscopy, and Thompson /12/ has employed matrix magnetic circular dichroism spectroscopy to study matrix isolated species. To date, few spectroscopic
techniques have not been applied to the matrix isolation technique.

Contemporary topics of matrix isolation studies are quite diversified. Bondybey /13/ has studied the photophysics of vibrational relaxation processes in matrix isolated \( C_3 \). Because of their potential as candidates for active mediums for new lasers, metal eximers have been studied by Andrews /14/ utilizing the matrix isolation technique since the van der Waals bound ground state is stable at low temperatures in an inert rare gas cage. Ozin /15/ has developed the cryophotoclustering technique which is a preparative route for generating transition metal clusters in a matrix. These studies will involve modeling clusters as active centers in dispersed heterogeneous catalysts. In the future, the matrix isolation technique will undoubtedly entertain new innovative themes as well as continuing to serve as an invaluable tool in the characterization of novel compounds; the elucidation of reaction pathway sequences; and the understanding of the low temperature chemistry, the photochemistry, and the photophysics of solid state systems.

C. METAL—WATER CHEMISTRY

1. INTRODUCTION

Chemical research that addresses the exploration of metal atom chemistry and the characterization of small metal
atom clusters finds itself at the crossroads of several richly fascinating, intensely studied disciplines of contemporary significance /20/. In the past decade, great strides have been made in the fields of organometallic /21-26/ and surface /27-30/ chemistry. Both disciplines, by implicit design, hope to elucidate fundamental processes in the area of metal-catalyzed chemical reactions. Organometallic chemists study homogeneous (i.e., in solution) catalysts containing a coordinatively unsaturated metal center commonly made of one to five metal atoms; for example, the popular Wilkinson catalyst, $\text{RhCl(PPH}_3)_3$, is used for the homogeneous reduction of olefins. Surface chemists attempt to interrogate the interaction of chemisorbed molecules on infinite, perfectly arrayed structures as a first step in the understanding of heterogeneous catalysis. They find that kinks, steps, or irregularities on the perfect surface are necessary for more realistic modeling /31/. Industrial heterogeneous catalysts are often comprised of finely divided metal particles (containing 50 to 100 metal atoms) dispersed on an inert support medium such as silica or alumina. For instance, the Fischer-Tropsch /32, 33/ catalyst, interest in which has had a resurgence in view of its pertinence to the conversion of coal to methanol and higher M.W. fuels, is composed of microcrystals of transition metals, commonly iron, on silica. Common to all
three of these distinct yet overlapping disciplines, is an
interest in understanding chemical interactions with metal
systems whether the metal system is a small unsaturated
metal multimer, a metal microcrystal, or a kink in a metal
surface. Consequently, the investigation of metal atom
chemistry and naked metal clusters employing the matrix
isolation technique may significantly enrich the fields
of surface chemistry, organometallic chemistry, and cataly-
sis, since such research may attempt to model the descrip-
tion of chemisorption, the active metal centers in homo-
geneous catalysts, and the active sites on metallic micro-
crystals /34-38/.

2. PREVIOUS MATRIX ISOLATION STUDIES OF METAL
CHEMISTRY

The matrix isolation technique has proven to be a very
powerful tool in the investigation of metal atoms, metal
atom clusters, and their complexes with other molecules
isolated in rare gas supports. U.V.-VIS absorption spectra
for a number of matrix isolated metal dimers have been
reported: Group IIA and IIB homonuclear and heteronuclear
diatomics /39-41/, Pb_2 /42/, Bi_2 /43/, Ni_2 /44/, Mo_2 /45/, Fe_2 /45/, and Pt_2 /46/, for example. U.V.-VIS absorption
spectra for a number of higher order metal clusters isolated
in a rare gas solid have also been reported: Ni_3 /44/,
Cu_3,4 /47/, and Ag_3-6 /48/, for instance. The chemical
literature is replete with studies of chemical interactions of metal atoms with a wide variety of molecules cocondensed in rare gas solids. These have recently been exhaustively reviewed by Klabunde /49/.

3. MOTIVATION FOR INVESTIGATION OF METAL--WATER CHEMISTRY

A major research theme in Dr. Margrave's laboratory for the past several years has been the investigation of metal atom(dimer)-water molecule interactions utilizing infrared and e.s.r. matrix isolation spectroscopy. A select number of other isoelectronic Lewis bases (NH$_3$ and HF) were also investigated in a limited number of experiments. The impetus behind the interrogation of these chemical systems includes the normal interest expressed in metal atom(cluster) interactions with different molecules which serve as models for metal surface-water reactions and water-induced thin film impurities aforementioned as well as their significant role in a number of important commercial processes and a number of theoretical studies. The steam reforming process, for example, is of integral value in the Fischer-Tropsch process in that it converts the methane by-product to synthesis gas (H$_2$ + CO) by passing it with steam over a nickel-based catalyst. The involvement of the nickel metal is not well understood, but conceivably involves
the interaction of the water with active sites on the metal surface. With the advent of integrated circuit technology, there has been an expressed need to prepare ultra-pure silicon and other semiconductor materials; however, serious problems have been encountered during the purification processes since water-induced thin film impurities develop.

Although a large portion of the metal atoms are quite reactive on a molecular scale (e.g., the Group IA metals) with water, even at cryogenic temperatures, chemical reactivity can be considerably quenched. In fact, it is well established that matrix isolation is suitable for studying reaction intermediates by cryogenically quenching and isolating them in an inert gas cage /35/. In 1970, \textit{ab initio} SCF MO calculations by Nicely and Dye /50/ on the Li\cdots NH$_3$ predicted a bound lithium-ammonia adduct by 20 kcal/mole. Since water is iso-electronic with ammonia, an investigation of the metal-water chemical systems could potentially reveal the existence of a novel class of molecular complexes. Subsequent to the experimental work, a large number of theoretical papers /51-57/ surfaced that addressed the nature of the bonding in the metal-water adduct because of its weak intermolecular noncovalent bonding properties as an electron donor-acceptor (EDA) complex /58,59/. 
As an additional incentive to study these chemical systems, it was believed that if the adduct could be quenched and isolated in the matrix cage, subsequent irradiation of the matrix solid could induce further reaction of the adduct on the ground state or an electronically excited state potential energy surface to form, in a labile fashion, new molecular species.

Therefore, because of their pertinence to surface chemistry, organometallic chemistry, heterogeneous catalysis, and a number of commercially significant industrial processes as well as their intrinsic chemical fascination, these metal-water experimental investigations were pursued utilizing infrared and e.s.r. matrix isolation spectroscopy.

The results of these experimental investigations are reported elsewhere /60-64/ and will therefore only be summarized below (see Figure I-1). A total of 26 metal atoms were studied: Li, Na, K, and Cs from Group IA /61, 62,65/; Mg, Ca, Sr, and Ba from Group IIA /60/; the first row transition metal series--Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn /60/; Al, Ga, In, and Tl from Group IIIA /60,64/; and Si, Ge, Sn, and Pb from Group IVA /60/.

Cocondensation of metal and water vapor in an argon matrix resulted in the formation of a one-to-one $\text{M}\cdots\text{OH}_2$ adduct for all the metals except for Ni, Al, Sc, Ti, and V. Al, Sc, Ti, and V spontaneously underwent oxidative
FIGURE I-1

BRIEF SUMMARY OF THE METAL-WATER MATRIX CHEMISTRY
insertion to form the divalent metal hydroxy hydride, HMOH. Ni simply did not form an adduct. Adduct formation was evidenced by a decrease in the $v_2$ bending mode frequency for H$_2$O at 1595 cm$^{-1}$ which ranged from 5 cm$^{-1}$ to 35 cm$^{-1}$. Photolysis of these adducts with light of wavelengths ranging from 300 nm to 600 nm induced the metal to insert into the OH bond to form the HMOH species except in the case of the Pb, Tl, and Zn adducts which remained as adducts after irradiation. In some cases, extended irradiation of the HMOH molecule induced homolytic cleavage of one or two of the hydrogen bonds to form the metal monohydroxide, MOH, or the metal monoxide, MO.

It was argued that the decrease in the $v_2$ bending mode frequency of water noted upon the formation of the one-to-one metal-water adduct is a probe of the degree of ligand → metal electron density transfer from the 3a$_1$ (σ lone pair that is partially bonding for the bent AH$_2$ molecule) water orbital to a metal atom orbital of A$_1$ symmetry which is consistent with a Lewis acid-base interaction. This interpretation parallels theoretical and experimental results which indicate that Li, Na, and Al metal atoms coordinate to H$_2$O through the oxygen to form an adduct of C$_{2v}$ symmetry with the metal atom becoming slightly negative /51-53, 62/. Photoelectron spectroscopy of H$_2$O by Potts and Price /66/ indicates that the bending mode frequency of H$_2$O$^+$ ($^2$A$_1$) decreases to 908 cm$^{-1}$
from 1595 cm\(^{-1}\) for neutral H\(_2\)O (\(^1\)A\(_1\)) when the 3a\(_1\) valence orbital is ionized (see Figure I-2) with a simultaneous enlargement of the bond angle to 180\(^\circ\). This suggests that electron density flowing from the 3a\(_1\) water orbital to a metal atom orbital of A\(_1\) symmetry will increase the bond angle with a concurrent decrease in the bending mode frequency. No changes in the stretching mode frequencies were observed. These considerations are consistent with a simple Walsh correlation diagram (see Figure I-3) type argument for an AH\(_2\) molecule where the a\(_1\) orbital is primarily nonbonding with some H-H bonding in the bent AH\(_2\) configuration and degenerate with the totally nonbonding b\(_1\) orbital when linear. Only the b\(_2\) orbital is A-H bonding in both dispositions (the a\(_1\) orbital is in the C\(_{2v}\) molecular plane along the C\(_{2v}\) axis; the b\(_2\) orbital is in the C\(_{2v}\) plane but normal to the C\(_{2v}\) axis; and the b\(_1\) orbital is normal to both the C\(_{2v}\) molecular plane and axis).

Electronic energy transfer or quenching processes have been a subject of study for the past half-century /67-69/. Most research efforts have focused on the quenching of the excited states of the Group IA alkali metal atoms, the Group IIB metal atoms (Zn, Cd, Hg), and the Group VIII rare gases by interaction with the ground states of a wide variety of atoms and molecules. There are a large number of transformations that may take place
FIGURE I-2

MOLECULAR ORBITAL DIAGRAM FOR
THE WATER MOLECULE
FIGURE 1-3

WALSH CORRELATION DIAGRAM FOR

THE AH₂ MOLECULE
upon interaction of an excited atom and a ground state species besides resonance fluorescence. For instance, the collision may induce spin-orbit relaxations; the electronic energy of the excited atom may be transferred to electronic and vibrational excitation in its collisional partner; or the interaction may be reactive generating new chemical species. This latter chemical type of exit channel is illustrated by the metathetical reaction of the triplet state of a Group IIB metal atom with paraffins /67,69/ (see Figure I-4).

\[ M(3P) + RH \rightarrow MH(2X) + R(2X). \]

Breckenridge /70/ postulates that coupling into the chemical exit channels results from adiabatic and/or diabatic traversals of chemical interaction surfaces of the type R-M-H, i.e., alkyl metal hydrides.

Quite recently matrix isolation photosensitized metal atom chemistry studies have helped delineate new photochemical pathways for the reactions of metals codeposited with alkanes. Margrave, et al. /71/ have reported the photosensitized reaction of a number of transition metals (Mn, Fe, Co, Cu, Zn, Ag, and Au) with methane in an argon matrix solid finding that the excited metal atom inserts into the C-H bond to form the methyl metal hydride, \( \text{CH}_3\text{MH} \); however, Ca, Ti, Cr, and Ni failed to yield insertion products. Ozin /72/ noted that continued irradiation
FIGURE I-4

SCHEMATIC DIAGRAM OF THE ENTRANCE AND EXIT
CHANNELS FOR ATOMIC EXCITED STATE
QUENCHING BY PARAFFINS
of the CH₃CuH molecule caused homolytic cleavage of the 
Cu-H bond and the Cu-C bond generating mostly CuH, some 
CuCH₃, and their respective radical products. This photo-
chemistry is particularly interesting since it involves 
the activation of saturated hydrocarbons which has com-
mercial significance /73,74/. However, it is also in-
teresting in that the RMH molecule postulated by Breck-
inridge as an intermediate in the chemical interaction 
of excited metal atoms with alkanes was quenched and 
isolated in the rare gas matrix cage.

From these studies the common aspects of matrix 
isoation metal atom photochemistry and excited state 
atom gas phase reactions are apparent since chemical 
exit channel pathways may be delineated. In the matrix 
cage, photochemically reactive reagents are already in 
juxtaposition so that photolytic activation of the metal 
atom and subsequent electronic quenching involving coupling 
into exit channels from traversals of chemical interaction 
surfaces may be studied step-by-step if small activation 
barriers are encountered at each crossing of the surfaces. 
Since the study of ground state metal atom chemistry in 
matrices with a wide variety of metals has already been 
established /49/, and these new investigations display 
the reactivity of excited state metal atoms with closed 
shell molecules, the future of employing matrix isolation 
spectroscopy to probe the reactivity of excited metal atoms
with other closed shell molecules to establish the excited state chemistry and generate and characterize a whole new host of chemical species seems very bright indeed. Only a handful of papers /62-64, 71,72/ have been published to date on matrix isolation metal atom photochemistry none of which employ U.V.-VIS spectroscopy. Therefore, a mapping of the electronic structures of these chemical systems is a field that is totally untapped and beckons to be explored.

There has been a recent flurry of theoretical interest in the interaction of electronically excited atoms with closed shell molecules. Interest in these chemical systems stems from a need to further understand weak intermolecular noncovalent forces /51,56,58,59/, to model bonding in heterogeneous catalysis systems /56,75/, to calculate cross sections for Penning ionizations /56,76/, and to evaluate the dynamics of gas phase atomic excited state reaction mechanisms /77/. These studies investigated electronically excited Li(2P) /51,56/, Be(3P) /56, 75,77/, Na(2P) /56/, and Ne(3P) /76/ atoms interacting with methane /77/, ethylene /51,75/, acetylene /75/, and water /51,56,76/ molecules finding that the potential energy wells are much deeper on some of the excited state electronic potential energy surfaces than their respective ground state surfaces and other excited surfaces some of which are even repulsive in nature. The energies of
stabilization for the excited state attractive interaction range from 5 kcal/mole to 33 kcal/mole (see Table I-1).

The experimental investigation of the exciplex (excited state complex) has always been of chemical interest /78/ especially in relation to their potential as active laser mediums /79/ in that their ground states are immediately depopulated by dissociation making population inverstion quite facile. Almost exclusively, however, their investigation has utilized the fluorescence technique which, although quite sensitive, can be blind to the detailed structure of the excited state of the complex if, for instance, intermultilet or vibrational relaxation is rapid, or if the excited state is unstable with respect to a chemical exit channel in which case no fluorescence would be likely to be detected. To properly assess the exciplex, the electronic structure must be explored directly with electronic absorption spectroscopy. The matrix isolation technique affords the unique opportunity to do this since sufficient concentrations of the complex are attained in the matrix to probe it with U.V.-VIS absorption spectroscopy. Such work will certainly be of interest in comparison to the ab initio calculations for the excited bound states of these complexes, in probing the nature of the electronic state that is unstable with respect to a chemical exit channel, in some
TABLE I-1

TABULATION OF THE RESULTS FOR THE AB INITIO
CALCULATIONS INVESTIGATING THE METAL-WATER
INTERACTION
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<td>(^2P)</td>
<td>(^2B_1)</td>
<td>(3s^23p^1(a_{1}^2b_{1}^1))</td>
<td>2.899</td>
<td>2.1</td>
</tr>
<tr>
<td>53</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>53,56</td>
<td>Al</td>
<td>(^2P)</td>
<td>(^2A_1)</td>
<td>(3s^23p^1(a_{1}^2a_{1}^1))</td>
<td>repulsive</td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>C</td>
<td>(^3P)</td>
<td>(^3A_2)</td>
<td>(2s^22p^2(a_{1}^2b_{1}^1b_{2}^1))</td>
<td>2.439</td>
<td>2.9</td>
</tr>
<tr>
<td>56</td>
<td>C *</td>
<td>(^1D)</td>
<td>(^1A_1)</td>
<td>(2s^22p^2(a_{1}^2b_{1}^2))</td>
<td>perhaps bound</td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>C *</td>
<td>(^1D)</td>
<td>(^1A_1)</td>
<td>(2s^22p^2(a_{1}^2b_{2}^2))</td>
<td>&quot;</td>
<td></td>
</tr>
</tbody>
</table>

* denotes excited state
instances, and in characterizing the electronic structure of the exciplex of interest.

D. MOLECULAR ORBITAL AND ELECTRONIC STATE CORRELATIONS

The investigation of chemical reaction dynamics occupies a central role in chemical research. Presently, there are a large number and a wide variety of quantum-chemical computational techniques of empirical, semi-empirical, and \textit{ab initio} natures that have been employed to quantitatively interrogate chemical reaction dynamics by mapping out the potential energy surfaces of chemical interaction. However, the success of utilizing molecular orbital and electronic state correlations to qualitatively predict or rationalize fundamental reaction dynamics for chemical systems is quite well established in the chemical community. Most notable is the work of Woodward and Hoffman that invokes conservation of orbital symmetry arguments to predict and explain chemical reactivity of principally organic reagents /80/. Orbital and state correlations have also been quite successful in rationalizing the results of ion-beam scattering experiments that investigate gaseous ion-molecule collisional processes /81-83/. The wide range success of the orbital and state correlations in understanding gaseous ion-molecule interactions stems partially from the
simplicity of these chemical systems that often involves an atomic ion interacting with a diatomic or very small polyatomic species in a bimolecular collision that sustains a particular geometry during the course of the interaction so that a particular set of symmetry elements is preserved. A small reaction complex has more discrete electronic structure which often implies unambiguous state and orbital correlations. From the electronic structure of the sample reactants and products, derived from electronic and photoelectron spectroscopy, the qualitative nature of the interaction potential energy surfaces may be derived which, in turn, predicates the chemical reaction dynamics. Certainly, the metal-water neutral interactions constitute simple chemical systems in that the reaction complex is composed of only four atoms, a simple geometry of approach may be assumed which is described by the $C_{2v}$ or the $C_s$ point group, and the electronic structure of the reactants are very well documented by optical and photoelectron spectroscopy and quantum-chemical calculations. Therefore, by resorting to molecular orbital and electronic state correlation methods, the photochemical reaction dynamics of the metal-water interactions may be investigated to understand relative reactivities, photochemical pathways, and chemiluminescent processes.
E. SUMMARY AND OVERVIEW

In view of the infrared matrix isolation studies of the metal atom-water molecule chemical systems and their subsequent photochemistry; the interest in this photochemistry as it relates to the activation of saturated molecules and the understanding of chemical quenching of gas phase atomic excited states; the \textit{ab initio} calculations of the excited state complexes; and the dearth of experimental electronic absorption data for exciplexes; it is of considerable interest to study the electronic absorption spectroscopy of the hydration reaction intermediates and the subsequent photolysis products of a wide variety of metal atoms. This thesis reports investigations of the Group IIA metal atoms (Mg, Ca, Sr, Ba), the Group IIIA metal atoms (Al, Ga, In), and the Group IVA metal atoms (Si, Ge, Sn, Pb) isolated in rare gas matrices with water at about 15 K. This study will be a useful adjunct to the infrared work which was motivated by its relevance to the varied disciplines of surface chemistry, organometallic chemistry, and heterogeneous catalysis. A mapping of the electronic structures of metal-water adducts could provide a better understanding of the nature of the chemical exit channel, thereby elucidating photochemical pathways important in saturated
bond activation and quenching of excited atomic states. Exploration of the electronic structures of the exciplexes would not only provide a reference data set to which future theoretical calculations may be compared but would also more reliably detail the features of the different excited states of the complexes. Further characterization of the photolysis products (HMOH, MOH, MO) is of basic chemical interest since many of these species are novel and hence undocumented spectroscopically. In addition, this thesis reports the study of the electronic structures of the Group IIIA metal suboxides (Al₂O, Ga₂O and In₂O) in absorption and emission. Interest in these high temperature molecular species stems from previous research efforts sporadically extending back over a generation that were partially unsuccessful in establishing the fundamental vibrational frequencies for these species in their ground states. Vibronic progressions in the bending mode and the symmetric stretch were noted in emission and absorption in this study of the metal suboxides. Finally, the electronic structures of several previously undocumented metal dimers were studied because of their relevance to catalysis.
REFERENCES


65. R.H. Hauge and J.L. Margrave, unpublished results.


CHAPTER TWO

APPARATUS CONSTRUCTION
CHAPTER TWO

OUTLINE

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A. INTRODUCTION

The final design of the ultraviolet-visible matrix isolation apparatus employed in the studies discussed in this thesis incorporated features common to most matrix isolation experimental setups as well as a number of unique aspects that abbreviated data acquisition time, obviated several experimental problems that have plagued other matrix isolation studies, and allowed for flexibility regarding the type of detection technique one might use to probe the isolated species. These particular aspects will be highlighted when appropriate in the forthcoming categorical discussion of the U.V.-VIS matrix isolation apparatus.

The experimental setup consisted of the following components: (1) the vacuum assembly, (2) the cold block, (3) the dual oven assembly, (4) the gas handling system, (5) the ultraviolet-visible spectrometer, and (5) the fluorescence spectrometer.

B. THE VACUUM ASSEMBLY

1. THE PRIMARY VACUUM CHAMBER

The vacuum assembly, depicted in Figure II-1, is
FIGURE II-1
SIDE VIEW SCHEMATIC DIAGRAM OF THE MATRIX ISOLATION VACUUM ASSEMBLY

A. DISPLEX CLOSED-CYCLE HELIUM REFRIGERATOR EXPANDER HEAD
B. HIGH PRESSURE HELIUM LINES
C. ELECTRICAL BNC VACUUM FEEDTHROUGHS
D. LIQUID NITROGEN PORT
E. TOP ALUMINUM FLANGE
F. PYREX GLASS OUTER VACUUM VESSEL
G. STAINLESS STEEL LIQUID NITROGEN DEWAR
H. COLD STATION ON THE SECOND STAGE OF THE CLOSED-CYCLE HELIUM REFRIGERATOR
I. COPPER INNER VACUUM AND RADIATION SHROUD
J. UV GRADE QUARTZ OPTICAL WINDOW
K. 50 OHM HEATING ELEMENT
L. ALUMINUM COLD BLOCK
M. SINGLE CRYSTAL SAPPHIRE SUBSTRATE ALUMINIZED ON THE SECOND SURFACE
N. QUARTZ CRYSTAL MICROBALANCE
O. 68 OHM ALLEN–BRADLEY CARBON THERMOMETER
P. COPPER FOIL BEAM DEFINING BAFFLE
Q. STAINLESS STEEL HOST GAS CARRIER LINE
R. COPPER SHUTTER
S. STAINLESS STEEL GUEST GAS CARRIER LINE
T. SIDE ALUMINUM FLANGE
U. PYREX GLASS VIEWING WINDOW
V. RESISTIVELY HEATED TANTALUM FOIL OVEN ASSEMBLY WITH INNER CRUCIBLE
W. STAINLESS STEEL GUEST GAS CARRIER LINE
X. COPPER WATER-COOLED TUBING
Y. TITANIUM SUBLIMATION PUMP
Z. HOT-FILAMENT IONIZATION GAUGE TUBE
comprised of a primary vacuum chamber and a secondary vacuum and radiation shroud. The primary vacuum chamber, denoted by "F" in Figures II-1 and II-2, is a pyrex tempered glass, T-shaped, cylindrical vessel that is 45 cm high and 45 cm wide having a 15 cm i.d. with 1.3 cm thick walls. Three pyrex, cylindrical optical ports, that are 7.5 cm long with a 3.8 cm i.d., were blown into the midsection of the T-shaped vessel's wall so that the lines defined by the normals to the bases of the optical port cylinders are out 45° between adjoining ports as depicted in Figure II-2. Each opening of this vessel is flared outward to accommodate O-ring grooves so that O-ring gasket vacuum seals could be formed with metal flanges and optical quartz and pyrex windows. During the two years of operation, no problems were incurred with the pyrex glass vacuum shell; it proved to be a reliable, sturdy support providing very clean vacua as well as allowing visual contact with the secondary vacuum shroud and oven assembly which was quite convenient during various alignment procedures.

The flange, denoted by "E" in Figure II-1 and viewed from a topside perspective in Figure II-3, is 26 cm in diameter and made from 1.3 cm thick aluminum plating. Twelve apertures with accompanying O-ring grooves were machined into the topside of this flange in a circular array. Seven of these apertures were fitted with vacuum
FIGURE II-2
TOP VIEW SCHEMATIC DIAGRAM OF THE MATRIX ISOLATION VACUUM ASSEMBLY

A. SIDE ALUMINUM FLANGE
B. STAINLESS STEEL GUEST GAS CARRIER LINE
C. INNER ALUMINUM TUBE RIDING ON DOUBLE O-RING GASKETS
D. COPPER WATER-COOLED TUBING
E. RESISTIVELY HEATED TANTALUM FOIL OVEN ASSEMBLY
F. PYREX GLASS OUTER VACUUM VESSEL
G. STAINLESS STEEL GUEST GAS CARRIER LINE
H. COPPER SHUTTER ASSEMBLY
I. STAINLESS STEEL HOST GAS CARRIER LINE
J. RECTANGULAR COPPER PLATE
K. COPPER FOIL BEAM DEFINING BAFFLE
L. SINGLE CRYSTAL SAPPHIRE SUBSTRATE ALUMINIZED ON THE SECOND SURFACE
M. QUARTZ CRYSTAL MICROBALANCE
N. COPPER WIRE
O. APERTURE IN THE COPPER FLOOR PLATE OPENING TO THE TITANIUM SUBLIMATION PUMP
P. ALUMINUM COLD BLOCK
Q. STAINLESS STEEL LIGHT SHROUD
R. PHOTOLYSIS PORT
S. UV GRADE QUARTZ WINDOW
T. MONOCHROMATOR PORT
U. PMT PORT
FIGURE II-3

PHOTOGRAPH OF THE TOP ALUMINUM FLANGE

WITHOUT THE CRYOCOOLER ASSEMBLED
feedthroughs. Three of these feedthroughs, utilized to suspend the radiation shroud, were made from 0.75 in. NPT Swagelok fittings whose screw threads were turned down and bored out to a smooth shaft and tapered on the end to form a press-fit with small, 0.4 cm thick brass flanges to which they were ultimately silver soldered. The brass flanges were mated to the aluminum flange with O-ring gaskets. The modified Swagelok fittings were equipped with Teflon ferrules that form a compression seal against cylindrical Teflon sleeves which encompass three thin-walled, stainless steel tubes which function as liquid nitrogen ports as well as supports for the copper radiation shroud (see "D" in Figure II-1). Two of the other vacuum feedthroughs, utilized to provide the high amperage required by the titanium sublimation pump, are identical to the three described above except that they are smaller, and the Teflon sleeve surrounds a 0.5 cm diameter copper rod. Initially, these vacuum feedthroughs leaked slightly; however, a light application of high vacuum epoxy subjected to a subsequent bake out totally resolved this problem. The two remaining feedthroughs provide a vacuum interface for (a) 0.125 in. dia. stainless steel tubing that transports the host krypton gas inside the copper shroud and (b) a 0.125 in. dia. brass rod that functions as a mechanical lever to open and close the copper shutter. Both of these feedthroughs
are made from Cajon weld fittings bored and tapered to
form a press-fit with a small brass flange which is then
silver soldered and mounted on the O-ring gasket seated
in the O-ring groove of the large aluminum flange. Theive unused apertures are sealed with small brass flanges.

An aluminum cylinder eleven cm high with a six cm i.d.
was press-fit in and welded to the central aperture of the
aluminum flange. This piece serves as a vertical posi-
tioning collar and a support buttress for the closed-cycle
helium Displex expander head (see "A" in Figure II-1).
The expander head rides on a ball-race located at the top
of the aluminum collar allowing the head to be rotated a
full 360°; the vacuum seal is made by two O-rings radially
compressing against the polished inner diameter of the
collar as depicted in Figure II-1. Utilizing only a thin
veneer of high vacuum grease, no detectable degradation
of the vacuum could be noted upon rotation of the expander
head.

A second aluminum flange, denoted by "T" in Figure
II-1 and shown in full view in Figure II-4, serves as a
support for the gas handling system and the dual oven
assembly. Five 0.250 in NPT threads were drilled and
tapped on a 12 cm dia. bolt circumference equally spaced
in a semicircular array. Three of these holes are
serviced by 0.250 in. NPT Swagelok vacuum fittings with
FIGURE II-4

PHOTOGRAPH OF THE SIDE ALUMINUM FLANGE
Teflon ferrules that surround and vacuum seal three 0.250 in. stainless steel tubes which, in turn, transport a gaseous guest species to the copper shuttered port. A 0.250 in. NPT Cajon fitting vacuum seals a 0.125 in. brass rod that controls a secondary shutter to the oven assembly. The last 0.250 in. aperture is stoppered with a 0.125 in. NPT plug.

Two aluminum tubes (four cm i.d.; five cm o.d.) were welded to the aluminum flange. The axis of one tube is centered on and normal to the plane of the aluminum flange. The axis of the second tube forms a 76.5° angle relative to the plane of the aluminum flange and intersects the flange six cm below the first axis. Both tubes have two O-ring grooves machined into their inner diameters so that a second pair of aluminum tubes, having smaller o.d.s and supporting the oven assemblies, may slide on the O-ring gaskets seated in these grooves. Such an arrangement allows one to easily change or repair the ovens since it is not necessary to disassemble the flange. Potentially, therefore, two high temperature species may be deposited concurrently; however, during the course of this work, this potential was not realized, and the top aluminum tube was fitted with a plug that accommodated a 4.5 cm dia. pyrex window which served as a viewing port as depicted by "U" in Figure II-1.

The lower end of the T-shaped vessel is assembled to and supported by an aluminum spacing collar that is connected to a TMC six-inch gate valve which is followed by a
freon cooled baffle that prefaces a NRC six-inch oil diffusion pump that is backed by a Welch Duo-Seal (model No. 1397) rotary forepump.

The three optical ports are sealed with 6.5 cm dia. U.V.-grade Supracil quartz windows seated on O-ring gaskets. In this work, two of the ports accommodate the U.V.-VIS reflection spectrometer; the third port allows the focused beam of a 100 watt mercury short-arc photolysis lamp to access the sapphire substrate.

2. THE SECONDARY VACUUM AND RADIATION SHROUD

a. THE LIQUID NITROGEN DEWAR

The secondary vacuum and radiation shroud has three sections: the liquid nitrogen dewar, the copper octahedral secondary vacuum jacket, and the titanium sublimation pump. The liquid nitrogen dewar, denoted by "G" in Figure II-1, was constructed of two 0.2 cm thick stainless steel seamless cylinders having their different diameters placed in a concentric disposition and welded on the top and bottom to stainless steel discs having centralized apertures to allow clearance for the second stage of the closed-cycle helium refrigerator. The upper stainless steel disc has three orifices equally spaced on a 11.7 cm bolt circumference to which three 1.1 cm dia. thin-walled stainless steel tubes were welded. The nonwelded end of these tubes was silver soldered to the turned down end of another
thin-walled stainless steel tube having a 1.3 cm diameter. This outer tube was assembled to a Swagelok fitting with a Teflon sleeve aforementioned. The concentric arrangement of these two tubes allowed one to cool down the inner tube without significantly lowering the temperature of the outer thereby preserving the integrity of the high vacuum seal.

The liquid nitrogen dewar has a three liter capacity. Normally, three liters of liquid nitrogen were required to cool down the whole shroud assembly. A subsequent three liters of L-N₂ were required if the oven was operated below 500°C; five liters if operated between 500°C and 1000°C; and ten liters if operated between 1000°C and 1500°C. The oven was operated for four to five hours during the course of a twelve hour period of experimentation.

b. THE COPPER VACUUM JACKET

The octahedral secondary vacuum jacket, denoted by "I" in Figure II-1, is comprised of eight 0.3 cm thick rectangular copper plates, denoted by "J" in Figure II-2, assembled to 0.6 cm dia. copper posts which were connected to two octahedrally shaped 0.3 cm thick copper plates on the top and bottom of the posts such that without the rectangular plates, the assembly had a "rib cage" appearance. The upper octahedral plate, which has a large central aperture to allow clearance for the cold block, is bolted to the bottom of the dewar with a large lead foil gasket
interposed to insure that a good thermal bond is established.

The copper rectangular plates are easily disassembled and interchanged to allow for flexibility regarding the type of experiment one might wish to perform. During the course of this work, two of the plates were equipped with light shrouds for the U.V.-VIS spectrometer as denoted by "Q" in Figure II-2. A third plate has a 2.5 cm dia. aperture which served as a photolysis port. A fourth plate supports the shutter system on the outside and a beam defining baffle on the inside (see "H" and "K" in Figure II-2). The cold block could be cooled to 130K when the dewar was filled and the oven was not on; however, with the oven temperature elevated to 1500°C, the cold block temperature raised to about 150K with the shutter closed increasing to about 230K with the shutter totally open. The remaining four plates are unadorned and in conjunction with those described above, serve as a radiation shield, light shroud, and a secondary vacuum jacket.

c. **THE TITANIUM SUBLIMATION PUMP**

The titanium sublimation pump, denoted by "Y" in Figure II-1, is composed of a large copper cylinder, that is silver soldered to the lower octahedral copper plate, and a ball-shaped titanium sublimation source supported
off a copper disc which is assembled to the cylinder. The source was the Mini Ti-Ball (Model No. 916-0008) supplied by Varian that is capable of delivering 15.2 grams of titanium before replacement is necessary. A typical titanium deposition involved driving 46 amperes at 7.0 volts through the element for ten minutes which vaporized about 0.025 grams of titanium onto the wall of the copper cylinder. The liquid nitrogen cooled thin Ti veneer deposited on the wall served as an excellent "getter" for such gases as H₂, N₂, O₂, CO, CO₂ and H₂O. The Ti sublimation pump was rarely employed since the vacua achieved utilizing the diffusion pump and liquid nitrogen cooling were sufficient for matrix isolation experimentation.

Without liquid nitrogen cooling, vacua attained outside the shroud were about 3 x 10⁻⁷ torr; with liquid nitrogen cooldown, vacua of about 5 x 10⁻⁸ torr were achieved. These vacua were measured with a hot-filament ionization gauge tube positioned about five cms below the sublimation pump as depicted in Figure II-1. Inside the vacuum shroud, vacua of about 5 x 10⁻⁹ torr were realized with liquid nitrogen cooling of the shroud; operation of the Ti sublimation pump further enhanced the vacuum to about 1 x 10⁻¹⁰ torr. These vacua were measured utilizing a quartz crystal microbalance mounted on the cold block and cooled to 130K as will be described in the next section.
species is deposited every second at a pressure of 10^{-6} torr, vacua of 10^{-7} torr are sufficient for matrix isolation experimentation as long as the deposition rate of the rare gas host species is sufficiently high to isolate the contaminant "guest" at a ratio of better than 10,000 to 1; consequently, the sublimation pump was not employed.

C. THE COLD BLOCK

1. THE ALUMINUM COLD BLOCK

The cold block, denoted by "L", "P", and "A" in Figures II-1,2, and 5, respectively, and shown in detail in Figure II-6, measures 0.85 cm by 0.85 cm by 6.5 cm and is made out of Alcoa, commercially-pure 1100-F aluminum. The aluminum block was placed in good thermal contact with the cold station of the closed-cycle helium refrigerator by melting Wood's alloy into the cold station's #8-32 threaded hole, screwing in the #8-32 aluminum stud on the block, and allowing the alloy to solidify. Aluminum was chosen for the block material because of its high reflectivity deep into the ultraviolet region, and its relatively high thermal conductivity at about 200K which is necessary to quickly dissipate any heat load placed on the cold block from the laboratory environment. However, second surface aluminized sapphire mirrors were employed in lieu of polished aluminum as a reflection surface due to a greater throughput of ultraviolet radiation with the mirrors. In retrospect,
FIGURE II-5
SCHEMATIC DIAGRAM OF THE COLD BLOCK AND
THE QUARTZ CRYSTAL MICROBALANCE MOUNT

A. ALUMINUM COLD BLOCK
B. ETP COPPER PRESSURE PLATE
C. QUARTZ CRYSTAL WAFER
D. GOLD IMPRINTED ELECTRODE
E. SINGLE CRYSTAL SAPPHIRE SUBSTRATES
F. ETP COPPER PRESSURE CLIPS
G. ETP COPPER PRESSURE PLATE
H. QUARTZ CRYSTAL WAFER
I. BUNA-N O-RING PRESSURE GASKET
J. TEFLOM SLEEVED GOLD WIRE
K. ETP COPPER GROUNDING PLATE
L. INDIUM FOIL THERMAL GASKETS
FIGURE II-6

PHOTOGRAPH OF THE COLD BLOCK
it would have been more appropriate to have constructed the cold block of ETP or OFHC grade copper than the aluminum since these grades of copper have higher thermal conductivity values at 20°C (about 12 watts/cm-K compared to 2 watts/cm-K/l/), but the Al block functioned satisfactorily.

Assembled to the aluminum block is a heating element, a sapphire substrate, a carbon resistance thermometer, and a quartz crystal microbalance. The heating element, located just below the cold station on the cold block ("K" in Figure II-1), allows the experimenter to bring the cold block up to 42°C by placing a 6.5 volt potential across the element's leads.

2. THE SAPPHIRE SUBSTRATES

The sapphire substrates ("M" and "E" in Figures II-1 and 5), measuring 3.1 cm x 0.6 cm x 0.3 cm, are made of UV grade, single crystal material custom manufactured by Adolf Mellor. Single crystal sapphire was specifically chosen because of its 100- to 1000-fold greater thermal conductivity over that of the fused material. The sapphire substrates have been aluminized on one surface so as to serve as second surface mirrors upon which matrices may be deposited and U.V.-VIS reflection spectroscopy may be performed. The sapphire substrates have a six degree taper
across the 0.3 cm dimension so as to wash out interference patterns generated by the reflected light from the front and back surfaces of the mirrors. The substrates were thermally bonded to the aluminum block with indium foil gaskets compressed by ETF copper clips shown in Figure II-5.

Since the aluminum cold block accomodated three deposition substrates, potentially, three times the number of experiments may be performed for a given period of time compared to those matrix isolation systems that use a single window through which they pass the sample beam of their spectrometer. Scan times, not sample number, effectively became the limiting feature in regard to data acquisition. In a long term frame of reference, data acquisition time was significantly abbreviated.

3. THE CARBON THERMOMETER

A 0.25 watt, 68 Ω (at 298K) Allen-Bradley carbon resistor was sunk into a 0.3 cm diameter hole at the bottom of the aluminum cold block ("O" in Figure II-1) and thermally bonded to the block by immersion into a pool of melted and subsequently resolidified Wood's alloy. The carbon resistor served as a very cheap, convenient, and highly reliable probe of the temperature of the cold block at cryogenic temperatures. The carbon thermometer is calibrated against a chromel vs. gold-0.07% at. Fe thermo-
couples, and Figure II-7 shows a plot of \( \ln R \) vs. \( \ln T \) for this particular thermometer. Carbon resistance thermometry is well documented and known to be quite accurate /2-4/.

4. **THE QUARTZ CRYSTAL MICROBALANCE**

A quartz crystal microbalance (QCM) was mounted and centered on one face of the aluminum cold block to provide a direct and accurate measure of the deposition rates for the host, guest, and contaminant species on the sapphire substrates. Accurate knowledge of these parameters is particularly useful in metal cluster studies since integrated peak intensities can be directly related to the metal atom flux with the other experimental conditions remaining the same. During the course of concentration variations, if a peak grows in according to the second, third, or fourth power of the deposition rate of the metal, it corresponds to the dimer, trimer, or tetramer, respectively.

A schematic diagram of the QCM mount is shown in Figure II-5. A piezoelectric quartz crystal wafer, with an AT-cut (39° 45') and two gold electrodes deposited on the two faces, is homogeneously compressed against a highly polished, ETP copper plate with a centralized aperture to prevent dampening of the oscillation ("K" in Figure
FIGURE II-7

LN(R) VS. LN(T) PLOT FOR THE CARBON THERMOMETER
\( \ln R (\Omega) \) vs. \( \ln T (K) \)

68 \( \Omega \) Carbon Resistor
Pressure is applied to the peripheral edge of the quartz crystal (QC) by a second polished copper plate ("G" and "B" in Figure II-5) through a Buna-N rubber O-ring gasket. The inner face of the QC is grounded out to the copper surface while the opposite face is in electrical contact with a Teflon coated, 0.005 inch dia. gold wire that is connected to an Inficon, Inc. (Model No. 007-029) oscillator drive circuit through a self-built interface circuit. The frequency of oscillation is monitored by a seven digit Systron-Donner (Model No. 7014) frequency counter capable of reading down to 0.1 Hz at 6 MHz. The QC, purchased from Airco Temescal (Model No. SC-8009), is 1.5 cm in diameter, 0.025 cm thick having a resonant frequency of 6 MHz.

The QCM technique takes advantage of the fact that the resonance frequency of an AT-cut QC operating in a thickness shear mode diminishes in a predictable fashion when mass is allowed to adhere to one or both of its faces. The mass-frequency relationship is given by /5/,

$$\frac{\delta f}{f} = -k(\delta m/A)$$

(1)

where $\delta$ is the magnitude of the decrease in frequency, $f$ is the resonance frequency, $\delta m$ is the mass of deposit, $A$ is the exposed area of one face of the QC, and $k$ is a constant which depends on the thickness of the crystal and density of the quartz.
A cryogenically cooled QCM acts as a miniature cryo-
pump condensing out room temperature gases and high temp-
erature vapors impinging at its surface; consequently, in
matrix isolation experimentation, one can measure and ratio
the frequency changes as a function of time for the host,
guest, and contaminant species and thereby, utilizing
equation (1), establish highly accurate isolation ratios
after correcting for molecular weights. The $k$ constant
value for this particular crystal make obtained from the
factory is 13.5 cm$^2$/gram which, utilizing equation (1),
translates into a sensitivity of 25 ng/Hz assuming an
exposed area of 2.0 cm$^2$. After correcting for a background
frequency drift rate, a frequency stability of about one
Hz over several hours was easily established for the operation
of the QC at 15$^\circ$K.

The cryogenically cooled QCM may also serve as a quan-
titative probe of the background pressure in the vacuum
chamber since from equation (1) and the fact

$$\frac{\delta m}{\delta t} \propto P$$

it follows that

$$\frac{\delta f}{\delta t} \propto P \text{ or } \frac{\delta f}{\delta t} = CP$$

assuming that other parameters such as temperature and
geometry are held constant. This QCM vacuum sensor tech-
nique contains an intrinsic systematic error in that it
assumes all the gases have sticking coefficients of unity; however, for nearly all gases at 150K, this is not a bad assumption. From a series of pressure studies, the value of C at 150K for the QC employed in these experiments was determined to be about 1 x 10^5 where $\delta f/\delta t$ and P have units of Hz/sec and torr, respectively. Applications of the QCM at low temperatures have been previously documented /6,7/; however, this is apparently the first application of a cryogenically cooled QCM in matrix isolation experimentation.

D. THE DUAL OVEN ASSEMBLY

An oven assembly is shown in Figure II-8 and labeled "V" in Figure II-1. The oven itself was comprised of 0.001 inch thick tantalum foil spot welded on the edges to form a cylinder that was about four cm long with a one cm diameter. This cylinder was then spot welded on each end to a pair of 0.020 inch thick Ta strips which, in turn, were secured to water-cooled copper electrode plates with a pressure fit. These plates were silver soldered to 0.250 inch diameter copper tubing that conducted current to resistively heat the Ta shell oven as well as cold, distilled water to cool the electrodes. Low voltage, high amperage was provided by a 10-to-1 Central Electric Co. step-down transformer coupled to a Variac power rheostat on the primary. The copper tubing was inserted into
FIGURE II-8

PHOTOGRAPH OF AN OVEN ASSEMBLY
0.250 inch holes in a Teflon plug which was seated in a 1.5 inch NPT Swagelok fitting with Teflon ferrules forming a compression fit, vacuum seal. The Swagelok fitting was assembled to an aluminum tube that rides on a double O-ring gasket seal machined inside a second aluminum tube previously mentioned. The Teflon plug also served as a vacuum feed-through for a pair of Chromel vs. Alumel leads. When the oven was elevated above 1000°C, a second 0.001 inch Ta foil cylinder with a three cm dia. was suspended over the inner Ta foil oven with an insulating alumina spacing collar to serve as a heat shield. Since various crucibles were used, contingent upon the metal being vaporized, they will be discussed in the experimental section corresponding to each metal. One oven assembly, when employed, was directed normal to the plane defined by the sapphire substrate; the second oven assembly, that was normally employed, was directed below the first but formed a 76.5° angle with respect to the plane of the sapphire substrate: both were positioned six inches away from and directed toward the center of the sapphire mirror. The potential across as well as the current through the Ta oven were continually measured to indirectly monitor the faithfulness of the metal flux after a deposition rate had been established with the quartz crystal micro-balance.
E. THE GAS HANDLING SYSTEM

The gaseous guest and host matrix materials were introduced into the vacuum chamber and directed toward the sapphire substrates by the gas handling system. This system is constructed out of 0.250 inch stainless steel tubing coupled to two variable leak valves (Granville-Phillips Co.; Series 203) that allowed one to meticulously bleed in extremely small quantities of gas. There are two gas lines: one line is devoted to the host gas, and the second line is reserved for the guest species. The high pressure side of the host gas line is directly coupled to the lecture bottle of the host material through a regulator that maintains the pressure in the line at 1.4 atmospheres. The vacuum side of this line is subjected to a liquid nitrogen trap then introduced to the vacuum chamber through the top aluminum flange. The line is then passed into the inner vacuum shroud and splayed into two branches that terminate to form two jets separated by 1.8 cm which homogeneously spray the host material onto the sapphire substrate positioned four cm away ("I" in Figure II-1). During the work described in this thesis, the pressurized side of the guest species line mostly serviced water vapor and was, therefore, maintained at the vapor pressure of water at 0°C; an ice bath was employed to circumvent vapor pressure instabilities incurred by fluctuations in the
room temperature. The vacuum side of this line was also branched to form two, separately valved (Nupro) lines ("S" and "W" in Figure II-1) that were introduced into the vacuum chamber through the side aluminum flange that supports the oven assemblies. These two lines terminated to form jets positioned outside the copper shroud before the 6.3 cm x 0.9 cm shuttered slit. These jets were responsible for homogeneously spraying the guest species onto the sapphire substrate located about seven cm away. Only the bottom jet was utilized since it alone could access the whole sapphire substrate with the shutter partially closed to occlude the high temperature vapor beam from condensing on the upper half of the substrate as depicted in Figure II-1. Thermocouple gauges were positioned upstream from the jets on the vacuum side of both the guest and host gas lines to monitor the faithfulness of the gas flow rates after deposition rates had been established with the quartz crystal microbalance.

F. THE ULTRAVIOLET-VISIBLE SPECTROMETER

1. THE LIGHT SOURCE

The entire ultraviolet-visible spectrometer has been built from scratch and is comprised of a light source, a light gathering and focusing mirror scheme, a light dispersing element, a light detector, and a signal proces-
sing system. Since the work involves the electronic spectroscopic analysis of photolytically reactive species, it was necessary to design the spectrometer so the broad band radiation was dispersed before it was allowed to reflect off the sapphire substrate so as to minimize the amount of radiant energy circulating through the rare gas solid. Figure II-9 shows a schematic diagram of the U.V.-VIS spectrometer. A schematic outlay of the optical pathway of the spectrometer emphasizing the mirror scheme is shown in Figure II-10. There are two sources of light: (1) an air-cooled, 15 watt deuterium discharge lamp, and (2) a 50 watt tungsten-halogen incandescent lamp with a quartz envelope. The deuterium lamp, constructed entirely from UV-grade fused silica, provided a continuum from 180 nm to 400 nm totally devoid of any spectral line features; in this work, it was employed primarily in the 200 nm to 360 nm spectral region. The deuterium lamp (Baush & Lomb DE-50A) was driven by a Baush & Lomb regulated power supply normally associated with the Baush & Lomb Spectronic 505 spectrophotometer. The incandescent tungsten-halogen lamp, supplied by Oriel Co., Model No. 6332, had a 3270°K color temperature generating a featureless continuum in the 350 nm to 800 nm spectral region necessary for this work. The tungsten-halogen lamp was powered by a Hewlett-Packard 6263B, 200 watt, regulated DC power supply.
FIGURE II-9

SCHEMATIC DIAGRAM OF THE
U.V.-VIS SPECTROMETER COMPONENT ARRAY
2. **THE OPTICAL SCHEME**

The light gathering and focusing mirror scheme is depicted in Figure II-10. The optical design allowed ease in switching back and forth between the ultraviolet and visible spectral regions, preserved the fast f/3.8 speed of the grating monochromator, permitted double-beam operation, and enabled one to easily convert to emission detection as will be described in the fluorescence spectrometer section. The flat mirror labelled "T", which can be rotated to access either lamp, reflected the light from the source toward flat "R" which directed the beam toward the on-axis paraboloid mirror "S" that, in turn, brought the beam to a line-shaped focus at slit "M" filling the aperture. A light chopper (PAR, Model No. 125A), modified to accommodate two channels, was interposed between mirror "S" and slit "M". The chopper blade was constructed to split the single-beam into a double-beam that could be spatially distinguished at the slit focus. The blade chopped the two light beams at frequencies of 422 Hz and 506 Hz at the top and bottom halves of the slit, respectively, thereby generating sample and reference audio-modulated light beams that are subsequently dispersed by the grating monochromator. The dispersed output of the monochromator was intercepted by flat "L" which directed the light toward paraboloid "J" that focused and
FIGURE II-10
SCHEMATIC DIAGRAM OF THE SPECTROMETER'S
OPTICAL COMPONENT OUTLay

A. SINGLE CRYSTAL SAPPHIRE SUBSTRATE
B. PYREX GLASS VACUUM VESSEL
C. UV GRADE QUARTZ WINDOW
D. INTERFACE COUPLER AND FILTER TRAY
E. 2.5 CM BY 5 CM FLAT MIRROR
F. ALUMINUM PMT HOUSING
G. PMT
H. 8 CM DIAMETER PARABOLIC MIRROR - 11 CM F.L.
I. ALUMINUM CAST MONOCHROMATOR HOUSING
J. 8 CM DIAMETER PARABOLIC MIRROR - 15 CM F.L.
K. 3 CM BY 6 CM FLAT MIRROR
L. 2.2 CM BY 6 CM FLAT MIRROR
M. VARIABLE WIDTH SLIT
N. 8 CM BY 8 CM 21° OFF-AXIS PARABOLIC MIRROR - 27 CM F.L.
O. 2 CM BY 2 CM FLAT MIRROR
P. 7 CM BY 7 CM PLANE SQUARE GRATINGS
Q. DUAL CHANNEL LIGHT CHOPPER
R. 6 CM BY 6 CM FLAT MIRRORS
S. 11.5 CM DIAMETER PARABOLIC MIRROR - 17.5 CM F.L.
T. 6 CM BY 6 CM FLAT MIRROR
U. TUNGSTEN - HALOGEN INCANDESCENT LAMP
V. DEUTERIUM DISCHARGE LAMP
W. BRASS LAMP HOUSING
demagnified the vertically split slit image onto the sapphire mirrored substrate that, in turn, deflected the dual-beam toward the photomultiplier tube housing. The reflected radiation was subsequently gathered and refocused onto the photomultiplier tube's photocathode by paraboloid "H". All of the mirrors that are not components of the monochromator or the cold block, were custom manufactured by Optical Instruments Laboratory of Houston, Texas except for mirrors "J" and "H" which were salvaged from a previously discarded IR spectrometer. All the mirrors were front surface aluminized and subsequently coated with MgF₂, layered for optimal throughput at 2000 Å.

During cocondensation, shadowing techniques were employed, utilizing the copper shuttered slit, to selectively occlude the high temperature vapor guest beam, emanating from the crucible, from condensing on the top half of the sapphire substrate. In this manner, the rare gas host matrix solid, which was homogeneously deposited over the whole of the sapphire substrate, was referenced by the dual-beam spectrometer thereby circumventing the severe light scattering induced problems that normally plague the ultraviolet portion of matrix isolation spectra.

3. THE OPTICAL DISPERING ELEMENT

The radiation dispersing element was a Perkin-Elmer Model 210 grating monochromator which is a conventional
Littrow type (see Figure II-10) monochromator employing a 21° off-axis parabolic mirror that has a focal length of 26.7 cm. Plane square gratings, 6.86 cm x 6.86 cm, were assembled back-to-back such that either grating may be rotated into position using a knob protruding from the top of the monochromator making it very easy to switch back-and-forth between the ultraviolet and visible regions in the first order. The grating was totally filled resulting in a minimum effective focal ratio of f/3.8. The grating drive scan arced out a 15° to 53° angle of incidence relative to the collimated beam from the paraboloid. A cosecant grating drive mechanism provided for an abscissa which is linear in frequency (cm⁻¹). The slitwidths may be varied between zero and one cm and read to an accuracy of five microns.

The monochromator employed two gratings with blaze wavelengths of 2400 Å (2880 grooves/mm) and 5400 Å (1440 grooves/mm) to service the 2000 Å - 3600 Å and the 3600 Å - 8000 Å regions of the optical spectrum, respectively. Both gratings were purchased from Baush & Lomb. The UV grating (Part No. 303-1320) and the visible grating (Part No. 303-1319) have linear dispersions of 11.4 Å/mm and 21.5 Å/mm at their blaze wavelengths, respectively. Both of the gratings were calibrated with mercury emission lines from a low-pressure mercury line source. The emission energies were correlated to the dial readings on the grating drive with a least-means-square routine.
4. **THE LIGHT DETECTOR**

The light detector employed was a Hamamatsu R-928 photomultiplier tube whose photocathode has an 185 nm to 930 nm spectral response. The PMT was normally biased at about 550 volts during the UV scan and 400 volts during the visible scan with a Tennelec Model AEC-5000 power supply. A terminating resistance of 220 KΩ was chosen for the anode since this value maximized the signal-to-noise ratio without enlarging the time constant of the circuit beyond the necessary 500 Hz frequency response.

5. **THE SIGNAL PROCESSING ELECTRONICS**

The signal processing system consisted of two lock-in amplifiers (PAR; Models 128A and 186), a ratiometer (Evans Associates, Model 4122), and a chart recorder (Texas Instruments). The lock-in amplifiers were each referenced by the light chopper at one of the two frequencies corresponding to the sample and reference channels and were thus able to deconvolute the signals riding on the PMT output which were subsequently ratioed by the ratiometer whose logarithmic output drove a chart recorder. Time constants and scan speeds were adjusted to minimize the noise levels present.
G. THE FLUORESCENCE SPECTROMETER

1. THE OPTICAL OUTLAY

The fluorescence spectrometer optical outlay, depicted in Figure II-11, was very similar to and thus easy to convert from the U.V.-VIS spectrometer's optical scheme. The photomultiplier housing along with its light gathering optics was positioned before the monochromator slit which had previously served as a light source input port for the U.V.-VIS spectrometer. The fluorescence collection optics had a focal ratio of about f/10 which is not very fast. A fused silica lens could have been interposed between the sapphire substrate and flat mirror labelled "K" in Figure II-10 along with replacement of paraboloid "J" to improve the speed of the optics up to f/4, but during this experimentation, satisfactory signal-to-noise levels were readily achieved with the slower optics. About three hours were required to switch from one detection technique to the other.

2. THE LASER SYSTEM

The laser utilized to induce fluorescence in this work was a Chromatix CMX-4 tunable flashlamp pumped dye laser. Second-harmonic crystals were employed to access the 260 nm - 305 nm UV region. The laser beam, measuring 0.3 cm in diameter, was directed toward the center of the sapphire substrate through the fused-silica window labelled "R" in
FIGURE II-11

SCHEMATIC DIAGRAM OF THE
FLUORESCENCE SPECTROMETER COMPONENT ARRAY
Figure II-2. Further pertinent details concerning the operation of the laser will be developed in the experimental sections.

3. **THE BOXCAR INTEGRATOR**

Signal-recovery processing was achieved utilizing a self-constructed boxcar gated integrator. The gated integrator synchronously samples an input signal with an aperture or gate of variable time resolution that can be fixed at any point on or slowly scanned across the input signal in a time frame-of-reference. The signal passed through the aperture is applied to a variable time constant integrator, the output of which is the average of some number of repetitions of the input signal over the aperture duration. The final magnitude of the output is contingent upon the input signal, the relationship between RC and the aperture pulse-width, the number of repetitions, and the initial voltage on the capacitor. For a single pulse

\[ e_{out} = \int e_{in} dt, \quad RC >> \Delta t \]

where integration is performed over the pulse width, \( \Delta t \). Because the average value of the noise over a large number of repetitions is zero, a signal-to-noise ratio enhancement is effected in the averaged output. If the aperture is fixed on a single point of the input signal, the output
rises asymptotically towards the average value of the input signal at the sampled point. If the aperture is scanned across the input signal, the synchronous waveform is reproduced at the output at the scan rate.

The boxcar integrator was constructed from seven Evan's Associates modules that included two gated integrator modules (Model 4130), two ramp generators (Model 4152), two different programmable time delay modules (Models 4141 and 4141-1), and a ratiometer module (Model 4122). Figure A-1 in the Appendix shows a schematic diagram of the boxcar's modules and their respective interconnected addresses. The addresses have been wired so as to accommodate three gated integrators and three time delay modules; however, during this work, only two of each were purchased to provide two gated channels. The functions corresponding to the numbered and lettered addresses for each of these modules are well documented by brochures available from Evans Associates, P.O. Box 5055, Berkeley, CA 94705. Figure A-2 in the Appendix shows the address connections for the control board.

The following is a list of the salient characteristics of this particular boxcar integrator:

(a) Three channel capability
(b) Linear or exponential integration
(c) Single point analysis as well as waveform recovery
(d) 30 ns to 1 µs time delay with a nominal 120 ns initial delay
(f) 1 picoampere maximum leakage current out of a guarded capacitor

(g) $10^{-4}$ second time constant

(h) Low pass filter after the averaged output

(i) Ratiometer

In this work, the output of the photomultiplier tube was preintegrated over 25 μs with a simple preintegrator circuit before it reached the boxcar input. Preintegration was implemented at the expense of time-domain information; however, where only pulse-intensity information is desired, this technique is commonly applied to circumvent difficulties encountered with pulsed lasers and time-domain experiments such as radiofrequency interference, jitter between the trigger and laser pulses, and high frequency bandwidths. In this work, the 25 μs pulse was probed by the boxcar after a 6 μs delay from the laser trigger pulse with a 1 μs wide aperture. More specific information regarding the operation of the boxcar integrator will be developed in the experimental sections.

H. GENERAL EXPERIMENTAL

Condensations were made upon the second surface sapphire mirrors and generally required 15 minutes to execute. Deposition rates for the guest and host species were established prior to condensation with the quartz crystal microbalance, and the host-to-guest ratios will be reported for each
experiment. Deposition rates are reported in units of Hz/min. and represent average values established from a 10 to 30 minute integration. The deposition rate of the krypton host material was typically set at about 7000 Hz/min. since this rate represented the best compromise between good isolation conditions and low light scattering. The background drift rate was typically 0.5 Hz/min. with the shutter open. For a typical experiment, the frequency rate of change for the guest and host species translates into $5 \times 10^{-8}$ moles of guest material being dispersed in $5 \times 10^{-5}$ moles of solid krypton matrix material for a 15 minute period of co-condensation. After the deposition was completed, the cryogenic cooling assembly was rotated 180° on its ball-race so as to position the cryogenic solid admixture before the spectrometer for subsequent analysis.

Cryogenic temperatures were achieved with an Air Products Displex closed-cycle helium refrigerator, Model CS-202, that cooled the sapphire surfaces to $13^\circ$K to $17^\circ$K, depending on the radiant heat loads from the laboratory and oven. Total cooldown required one hour and 45 minutes to achieve, and the final temperature was continually monitored by the Allen-Bradley carbon thermometer sunk into the cold block whose resistance changed from $68\Omega$ at $298^\circ$K to $157\Omega$ at $13^\circ$K. The liquid nitrogen dewar was filled prior to commencing cooldown to drastically diminish the rate of outgassing from the inner copper vacuum shroud.
as well as to trap out the residual water vapor in the vacuum vessel. Without prior cooldown of the dewar, seeding sites formed on the sapphire substrate which generated highly light scattering, crystalline rare gas solids. Upon filling the dewar, the system's vacuum, as probed by the ionization gauge, lowered from $3 \times 10^{-7}$ torr to about $8 \times 10^{-8}$ torr finally stabilizing at about $5-7 \times 10^{-8}$ torr upon final cooldown of the cold block if the oven was not operating. During cooldown, however, the oven was generally operated to outgas the oven assembly and the high temperature guest material. The oven was always operated for at least two hours prior to deposition at temperatures that corresponded to $10^{-5}$ to $10^{-4}$ torr for the vapor pressure of the metal or high temperature species being investigated. The oven temperatures, when monitored, were measured with a Chromel vs. Alumel thermocouple seated at the rear of the crucible or, more commonly, with a Leeds & Northrup optical pyrometer. The oven's electrical power consumption was always measured which served as a reliable probe of how the oven was operating as well as a rough yet quite convenient value to relate to metal flux rates which could then easily be re-established on a day-to-day basis. The crucibles from which the metals were vaporized will be described in each experimental section.

High Purity Matheson research grade krypton and argon (99.995%), further purified by passage through a liquid
nitrogen trap, were used in all the experiments. Deionized tap water was used for the $\text{H}_2\text{O}^{16}$ source. $\text{D}_2\text{O}$ (98.8%) was purchased from Colombia Organic Chemicals Co., and $\text{H}_2\text{O}^{18}$ (95%) was procured from Prochem-Isotopes. Isotopes of water were used in a number of studies to aid in the assignment of some electronic transitions. All liquids were vacuum distilled going through at least five freeze-thaw cycles to degas the liquids of atmospheric gases. Metal sources and purities will be reported in their respective experimental sections.

The matrices were often photolyzed subsequent to trapping with a 100 watt, medium pressure, short-arc mercury discharge lamp whose radiant energy was directed through a fused silica optical port ("R" in Figure II-2) normal to the plane of the sapphire substrate and focused down to an one inch diameter spot. A Pyrex-water filter was often employed to extract infrared radiation and hence curb the heat load on the matrix. Photolysis times and long-pass Corning filters utilized in wavelength selective studies will be reported for each experiment. Occasionally, the monochromator with its slits widened was employed to photolyze selectively with the 50 watt tungsten-halogen lamp used as a radiation source, in which case, photolysis times and band passes will be reported for each experiment as well.
The matrices were routinely annealed for particular sets of experiments to eliminate unstable matrix sites as well as to help identify bands attributable to polymeric complexes of a particular monomer. The complex band is enhanced after the annealing process since diffusion of a monomer through a matrix is more efficient at a higher temperature in a resultant more malleable medium. Unfortunately, the originally glassy rare gas solid (which has a low light scattering character) becomes crystalline (actually clusters of microcrystals are formed) and hence highly light scattering after the warming cycle, thus, only a representative set of experiments were annealed. During the annealing process, the matrix is warmed to 420K from about 150K and then allowed to recool; the whole cycle requires about three minutes to execute.

The assignments for the electronic transitions are in general accurate to ±15 cm\(^{-1}\) as estimated from the calibration data. The resolution of the monochromator was always more than adequate since this work primarily investigated vibronic spacings and electronic transitions which for the latter's case in the solid state are typically quite broad (50 to 500 cm\(^{-1}\) except for the zero phonon lines which can be relatively sharp (~1 cm\(^{-1}\)). For example, at 18,250 cm\(^{-1}\) (5400 Å), the monochromator had a resolution of better than four wavenumbers while maintaining a signal-to-noise
ratio of well over 100-to-1. Since the vibronic spacings of metal dimers, which were studied in this work, are rarely less than 50 cm$^{-1}$, the resolution provided by the monochromator was quite satisfactory.

Normally, twelve hours were required to complete a full experiment that involved three depositions, three full scans (2000 Å to 8000 Å), selective photolysis, and subsequent selective scanning to evaluate the effect of photolysis. At the end of each day's experiment, the cold head was warmed by backfilling the vacuum vessel with a nitrogen or helium purge. Subsequently, the sapphire substrates were scrupulously cleaned utilizing HPLC methanol as a solvent and soft tissue as a mechanical buffing agent. Daily cleaning of the sapphire substrates was imperative since small clusters of the residual guest species were not only light scattering in themselves but also served as seeding sites from which light scattering, crystalline rare gas solids grew. The vacuum vessel was then sealed, evacuated with a rough pump, and pumped overnight by an oil diffusion pump before the ensuing experiment the next morning.
REFERENCES


CHAPTER THREE

ELECTRONIC MATRIX ISOLATION SPECTROSCOPIC STUDIES OF
THE GROUP IIA METAL-WATER PHOTOCHEMISTRY
CHAPTER THREE

OUTLINE

III. ELECTRONIC MATRIX ISOLATION SPECTROSCOPIC STUDIES
    OF THE GROUP IIA METAL–WATER PHOTOCHEMISTRY

    A. INTRODUCTION
    B. EXPERIMENTAL
    C. RESULTS
        1. MAGNESIUM AND WATER
        2. CALCIUM AND WATER
        3. STRONTIUM AND WATER
        4. BARIUM AND WATER
    D. DISCUSSION
        1. NATURE OF THE ELECTRONIC STATES OF THE
           GROUP IIA METAL WATER COMPLEXES
           a. PRELIMINARY CONSIDERATIONS
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III. ELECTRONIC MATRIX ISOLATION SPECTROSCOPIC STUDIES OF THE GROUP IIA METAL-WATER PHOTOCHEMISTRY

A. INTRODUCTION

There is a wide-ranging fascination with the molecular scale, theoretical and experimental investigations of the interactions of the Group IIA divalent metal atoms with other atomic and closed shell molecular species. Non-reactive ground state molecular interactions are interesting in that there is no formal chemical bonding involved so that the weakly cohesive attractions are primarily derived from London dispersive forces. However, electronic excitation of the IIA metal atom often leads to a significant enhancement of the bonding interaction with the other moiety such that these species may be categorized as excimers or exciplexes. Interest in these complexes is piqued by their potential as active laser mediums since population inversion is facile for species that are very weakly bound and hence dissociative in the ground state. The recent rare gas-halide excimer lasers illustrate this point and have sparked spectroscopic study of similar species. For instance, there have been extensive spectroscopic studies of the Group IIA heteronuclear and homonuclear diatomic species which have recently been reviewed by Miller and Andrews /1/. Additionally, there has been intense spectroscopic research aimed
toward understanding the chemical exit channels of photosensitized decomposition reactions of small polyatomic and diatomic molecules with excited Group II metals /2/. Along this vein, Mandl and Hyman have carried out gain/absorption measurements on the green emission from the \((\text{Hg}_2\text{NH}_3)^+\) exciplex to determine its potential as an energy storage laser /3/. Spectroscopic analysis of excimers and exciplexes will continue to be popular in view of the continuing search for different active laser mediums.

Reactive interactions of the Group IIA metals with small molecules have also been extensively studied along theoretical and experimental avenues. Theoretical studies have modeled chemical bonding on transition metal surfaces and clusters with the Group IIA metal-olefin interactions /4/. This research is motivated by the hypothesis that bonding in catalytic systems primarily involves the 4s and 4p orbitals of the transition metals in question with the d orbitals playing a minimal role /5,6/. Since beryllium can be treated with a fair degree of theoretical rigor, Swope and Schaefer have studied this atom interacting with an ethylene molecule with Be in its ground \(1S\) state and three-fold degenerate excited \(3P\) state. These calculations indicate that the ground state interaction is essentially repulsive, but the excited state interaction \(3\text{B}_2\) is rather well bound (19 kcal/mole). Such investigations
intimate the potential for photosensitized heterogeneous catalysis.

There have been a number of experimental and theoretical investigations of the Group IIA metal-water interactions. Kauffman /7/ has performed infrared matrix isolation studies on the IIA metal-water interactions demonstrating that initially a weakly-bonded metal-water adduct could be trapped in the matrix upon cocondensation as evidenced by a decrease in the ν₂ bending mode frequency of water. Experimental results suggest that the bonding of the metal-water complex involves an interaction through the oxygen of water. Selective photolysis of the rare gas matrix employing Corning cutoff filters induced the metal to oxidatively insert into the O-H bond of water to form the hydroxy metal hydride, HMOH, for Mg, Ca, Sr, and Ba metal atoms. In addition to HMOH, the metal monohydroxide, MOH, was generated upon irradiation of the strontium- and barium-water adducts. Continued photolysis of the matrix with ultraviolet radiation (λ > 3000 Å) was unsuccessful in photodissociating any of these products. Theoretical investigations have evaluated the M-O bond distances and energies of dissociation for the metal-water adduct with the metal in its ground and excited states, as well as the equilibrium conformations for the HMOH molecule. Bentley /8/ has examined the ground state interactions of
Be and Mg with water in a $C_{2v}$ point group and finds that the bonding is essentially nonexistent; however, he reports that the bonding of Be···OH$_2$ in the $^3B_2$ excited state is attractive by about 19 kcal/mole. Curtiss and Frurip /9/ have calculated the bonding interactions of the adducts for beryllium and magnesium to be 0.62 and 2.33 kcal/mole, respectively, which can be accounted for in terms of dispersive forces. They find definite minima in the potential surfaces for these adducts that correspond to a $C_{2v}$ configuration for Mg···OH$_2$ and a $C_s$ configuration for Be···OH$_2$ with the Be atom above the plane defined by the water. Curtiss and Frurip /9/ also calculated bond distances and geometries for HMgOH and HBeOH and report that HMgOH is linear while HBeOH has a BeOH bond angle of 145°. These investigators also carried out limited calculations that indicated there is a potential energy barrier to insertion which they believe is apparently overcome by the energy provided in photolysis so the reaction follows a ground state potential energy surface.

In view of these fascinating investigations of the Group IIA metal atom chemistry as they relate to the spectroscopic characterization of exciplexes, theoretical modeling of heterogeneous catalysis with hints of photoactivation, and detailed experimental and theoretical exploration of the metal-water interactions
and reactions, it is of considerable interest to probe the electronic structures of the Group IIA metal atom hydration reaction intermediates and products isolated in rare gas matrices. Such an investigation may be of assistance in (1) elucidating the nature of the photochemical exit channels pursued on a collision of an excited Group II metal atom with a small molecule, as well as (2) characterizing the detailed electronic structure of the exciplex thereby providing a data bank to which future theoretical calculations may compare. This study will also form a useful adjunct to the previous infrared matrix isolation studies since it will examine the perturbations of the electronic structure of metal atoms upon interaction with the water molecule as well as possibly characterize new reaction products not apparent in the infrared studies. Molecular orbital and electronic state correlation diagrams will be employed to help understand the photolytically induced reaction pathways and the electronic structures of the intermediates. Additionally, the electronic spectra of the Ba atom and dimer will be presented and discussed since previous studies /10/ were quite tentative in their assignments.
B. EXPERIMENTAL

Purified grade magnesium metal was obtained from J.T. Baker. Purified calcium metal was procured from Sargent-Welch, SC1190. Both the strontium and the barium metals were acquired from Alfa Ventron at 99.99% purity. All four metals were vaporized from a stainless steel crucible at temperatures that correspond to a vapor pressure of about $1 \times 10^{-4}$ torr for the metal investigated. Thirty-mil thick carbon cloth was wrapped around the crucible to insulate it electrically from the Ta foil furnace assembly. The furnace assembly was outgassed for two hours prior to deposition at temperatures about 50 degrees below that used during deposition. Guest-to-host ratios for the metal and water were accurately evaluated by measuring the deposition rates for krypton, water, and the metal of interest with the quartz crystal microbalance and will be reported for each experiment. Each matrix sample preparation required a 15 minute deposition. Selective photolysis studies employed the monochromator used in the spectroscopic studies having its slits widened to allow a 20 Å bandpass with a tungsten-halogen light source. Photolysis times and wavelengths will be reported for each experiment.
C. RESULTS

1. MAGNESIUM AND WATER

Cocondensation of magnesium metal vapor with water vapor on a sapphire substrate maintained at 15 K in an excess of krypton generates a transparent, colorless matrix.

Figure III-1 shows two electronic absorption spectral traces corresponding to two experiments: Mg/H$_2$O/Kr and Mg/H$_2$O/Kr + hv. Table III-1 lists the assignments corresponding to band maxima for each of these spectra. The assignments are made after the matrix has been annealed to 42 K over a period of three minutes. The annealing process was effective in sharpening some of the bands with corresponding minor red and blue shifts in band positions. Band "A" in trace A corresponds to a strongly allowed electronic resonance transition for the Mg metal atom since this is the only band that persists in high dilution studies of Mg in Kr without water. Comparison of this band energy with gas phase transition energies for Mg /11/ allows the assignment of band "A" to the 3s3p($^1$P) + 3s$^2$(1S) atomic resonance transition of Mg. The major "A" band is only slightly blue shifted (20 cm$^{-1}$) relative to the gas phase transition and is triplet in structure. This absorption spectra is in excellent agreement with those of other authors /12,13/. Although various theories have been projected to explain the triplet structure of this $^1$P + $^1$S transition (e.g.,
FIGURE III-1

ELECTRONIC ABSORPTION SPECTRA FOR MAGNESIUM AND WATER ISOLATED IN A KRYPTON MATRIX

TRACE A \quad \text{Mg:}H_2O:Kr = 1:50:1550

TRACE A' \quad \text{Same as trace A but photolyzed for two seconds with light of } \lambda > 3200 \text{ Å}
KRYPTON MATRIX

Mg + H₂O + hν(†)

λ ≥ 3200 Å

ABSORBANCE

CM⁻¹ (x10⁻³)


**TABLE III-1**

**ASSIGNMENTS FOR THE OPTICAL ABSorption SPECTRA**

**OF THE Mg/H\textsubscript{2}O/Kr AND Mg/H\textsubscript{2}O/Kr+h\nu SYSTEMS**

<table>
<thead>
<tr>
<th>Peak</th>
<th>λ(Å)</th>
<th>ν(cm\textsuperscript{-1})\textsuperscript{a}</th>
<th>Species</th>
<th>Assignment\textsuperscript{c}</th>
<th>Gas Phase\textsuperscript{b} (cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2854</td>
<td>35 032</td>
<td>Mg</td>
<td>3s3p(^1\text{P}) + 3s(^2\text{S})</td>
<td>35 051</td>
</tr>
<tr>
<td>B</td>
<td>3326</td>
<td>30 068</td>
<td>Mg\textsubscript{2}OH\textsubscript{2}</td>
<td>(^1\text{B}_2) &amp; (^1\text{B}_1) + X((^1\text{A}_1))</td>
<td>?</td>
</tr>
</tbody>
</table>

\textsuperscript{a} ± 15cm\textsuperscript{-1}.

\textsuperscript{b} From ref. 11.

\textsuperscript{c} Energies of transition are taken from band maxima unless noted otherwise.
multiple trapping sites, metal-metal interactions, crystal field effects, etc.), a recent magnetic circular dichroism (MCD) study /14/ of Mg in various inert gas matrices indicates that the characteristic triplet structure arises from Mg atoms at a single site and can probably be interpreted in terms of a Jahn-Teller effect assuming an octahedral site symmetry. No other atomic transitions were observed.

Because it grew in as a consequence of increasing the water concentration, the band denoted by "B" in trace A may be assigned to the reaction product of magnesium and water which, in collaboration with previous infrared studies /7/, may be identified with the 1:1 magnesium-water adduct. High water dilution studies failed to change the structure of band "B" thereby eliminating the possibility of a higher order metal-water interaction causing the broad character of this band which has a red onset at about 27,000 cm\(^{-1}\) and a blue cutoff at about 32,000 cm\(^{-1}\). Irradiation of the matrix sample with light of \(\lambda > 5000 \text{ Å}\) (CS 3-70 and Pyrex-water filters) for ten minutes does nothing to destroy the integrity of the "B" band. A one-half second photolysis with light of \(\lambda > 3200 \text{ Å}\) (CS 1-64 filter) destroys about 30% of the intensity of band "B". Trace A' in Figure III-1 shows that a two second photolysis with the same color light totally eliminates the adduct
band without subsequent generation of any new absorption bands between 210 nm to 800 nm. The final photolysis product observed in the infrared studies was H\textsubscript{2}MgOH which probably has its first electronic transitions in the ultraviolet region. Irradiation of the matrix causes a slight red shift in the "A" band which is probably attributable to a photo-induced annealing process. With the consideration that the infrared studies show that the adduct is initially formed upon cocondensation, and that the "B" band displays very similar photosensitivity as the adduct band did in the infrared work, the assignment of the "B" band to the metal-water complex is quite plausible.

2. CALCIUM AND WATER

Cocondensation of calcium and water vapor on a sapphire substrate maintained at 15 K in an excess of krypton generates a transparent, red matrix.

Figure III-2 shows an electronic absorption trace corresponding to one experiment: Ca/H\textsubscript{2}O/Kr. Figure III-3 shows five expanded scale absorption traces corresponding to the Ca/H\textsubscript{2}O/Kr matrix sample being selectively photolyzed with different wavelengths of light. Table III-2 lists the assignments corresponding to the band maxima for each of these spectra. The assignments were made after the matrix had been annealed to 42 K over a period of about three
FIGURE III-2

ELECTRONIC ABSORPTION SPECTRUM FOR CALCIUM AND WATER
ISOLATED IN A KRYPTON MATRIX

Ca:H₂O:Kr = 1:60:3700
FIGURE III-3
EXPANDED SCALE ELECTRONIC ABSORPTION SPECTRA FOR CALCIUM
AND WATER ISOLATED IN A KRYPTON MATRIX WITH
SELECTIVE PHOTOLYSIS

TRACE A - Ca:H₂O:Kr = 1:60:3700

TRACE A' - Same as trace A but photolyzed for 40 minutes with light of λ = 5237 Å
- 5257 Å

TRACE B - Same as trace A but photolyzed for 30 minutes with light of λ = 4698 Å
- 4718 Å

TRACE C - Same as trace A but photolyzed for 30 minutes with light of λ = 4813 Å
- 4833 Å

Trace C' - Same as trace C but photolyzed for 15 minutes with light of λ = 4953 Å
- 4973 Å
TABLE III-2
ASSIGNMENTS FOR THE OPTICAL ABSORPTION SPECTRA
OF THE Ca/H$_2$O/Kr AND Ca/H$_2$O/Kr + hv SYSTEMS

<table>
<thead>
<tr>
<th>Peak</th>
<th>$\lambda$(Å)</th>
<th>$\bar{v}$(cm$^{-1}$)$^a$</th>
<th>Species</th>
<th>Assignment$^c$</th>
<th>Gas Phase$^b$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4209</td>
<td>23 756</td>
<td>Ca</td>
<td>$4s4p(^1P) \rightarrow 4s2(^1S)$</td>
<td>23 652</td>
</tr>
<tr>
<td>A</td>
<td>4277</td>
<td>23 378</td>
<td>Ca</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>B</td>
<td>4582</td>
<td>21 826</td>
<td>Ca</td>
<td>$4s3d(^1D) \rightarrow 4s2(^1S)$</td>
<td>21 850</td>
</tr>
<tr>
<td>C</td>
<td>4705</td>
<td>21 256</td>
<td>Ca···OH$_2$</td>
<td>$C(^1B_1) \rightarrow X(^1A_1)$</td>
<td>?</td>
</tr>
<tr>
<td>D</td>
<td>4809</td>
<td>20 794</td>
<td>Ca···OH$_2$</td>
<td>$C(^1B_1) \rightarrow X(^1A_1)$</td>
<td>?</td>
</tr>
<tr>
<td>E</td>
<td>4947</td>
<td>20 215</td>
<td>Ca···OH$_2$</td>
<td>$B(^1A_1) \rightarrow X(^1A_1)$</td>
<td>?</td>
</tr>
<tr>
<td>F</td>
<td>5231</td>
<td>19 116</td>
<td>Ca···OH$_2$</td>
<td>$A(^1B_2) \rightarrow X(^1A_1)$</td>
<td>?</td>
</tr>
<tr>
<td>G</td>
<td>6906</td>
<td>14 480</td>
<td>Ca$_2$</td>
<td>$A(^1\Sigma^+_u) \rightarrow X(^1\Sigma^+_g)$</td>
<td>~15 150$^d$</td>
</tr>
<tr>
<td>H</td>
<td>7178</td>
<td>13 931</td>
<td>Ca$_2$···OH$_2$</td>
<td>$A \rightarrow X$</td>
<td>?</td>
</tr>
<tr>
<td>I</td>
<td>3794</td>
<td>26 357</td>
<td>Ca$_2$</td>
<td>$^1\Pi_u \rightarrow X(^1\Sigma^+_g)$</td>
<td>~26 700$^{d,e}$</td>
</tr>
<tr>
<td>J</td>
<td>5517</td>
<td>18 126</td>
<td>CaOH</td>
<td>$B(^2\Sigma^+) \rightarrow X(^2\Sigma^+)$</td>
<td>?</td>
</tr>
<tr>
<td>K</td>
<td>6213</td>
<td>16 096</td>
<td>CaOH</td>
<td>$A(^2\Pi) \rightarrow X(^2\Sigma^+)$</td>
<td>?</td>
</tr>
<tr>
<td>L</td>
<td>6359</td>
<td>15 727</td>
<td>CaH</td>
<td>$B(^2\Sigma^+) \rightarrow X(^2\Sigma^+)$</td>
<td>15 755$^d$</td>
</tr>
</tbody>
</table>

$^a$ ± 15 cm$^{-1}$.

$^b$ From refs. 1, 11, and 16.

$^c$ Energies of transition are taken from band maxima unless noted otherwise.

$^d$ $\nu_{00}$.

$^e$ In an argon matrix.
minutes. The annealing process was effective in sharpening some of the bands with corresponding minor red and blue shifts in positions. The bands denoted by "A" and "B" in Figure III-2 can be attributed to atomic resonance transitions for calcium since only these bands persist during the course of high Ca dilution experiments without water. Previous absorption, emission, and MCD /15/ studies of Ca atoms in inert matrices are in excellent agreement with these spectra and have established the nature of the observed transitions. From these studies, bands "A" and "B" are assigned to the $4s4p(^1P) + 4s^2(^1S)$ and the $4s3d(^1D) + 4s^2(^1S)$ Ca atomic resonance transitions. The MCD study has unequivocally established that the absorption doublet observed in the "A" band is due to the Ca atom residing in two different sites in the rare gas solid. The more important role that multiple sites play in Ca than Mg precluded a MCD analysis of the characteristic triplet observed in the major "A" band of Ca. The $^1D + ^1S$ assignment to the "B" band has been questioned since it is a rather intense band for a parity forbidden atomic transition. However, this assignment has been bolstered by the MCD study /15/ that concludes it is likely that the $^1D + ^1S$ intensity is borrowed from the $^1P + ^1S$ transition via a static site mechanism where the site symmetry has no center of inversion and is sufficiently high to resolve the components of the P and D states into
the same irreducible representation to permit intensity borrowing. Andrews et al. [15] suggest that a $D_{3h}$ site symmetry is the most reasonable in a krypton solid. No other atomic transitions were observed. The bands denoted by "G" and "I" are assigned to electronic transitions of the calcium dimer, since upon increasing the Ca concentration, these bands are the first to grow in after the atomic bands and display a quadratic intensity dependence on the metal deposition rate. The "G" band shows a vibronic progression with $\Delta G'_{v+1} = 119 \text{ cm}^{-1}$. The "G" and "I" bands have been quite extensively studied in the gas and solid phases [1] and are assigned to the $A(1\Sigma_u^+) + X(1\Sigma_g^+)$ ($\omega_e = 118 \text{ cm}^{-1}$ in krypton) and the $1\Pi + X(1\Sigma_g^+)$ transitions for Ca$_2$, respectively.

The bands denoted by "C", "D", "E", and "F" may be assigned to the 1:1 reaction product of calcium and water since these bands are the first bands to grow in as a consequence of doping the matrix sample with water and maintain identical relative intensities with different water dilutions. In collaboration with the previous IR studies [7], these bands may be identified with the calcium-water adduct, Ca···OH$_2$. From Ca concentration studies, it is apparent that the "H" band also grows in as a consequence of water doping but only if there is some calcium dimer present in the matrix; consequently, the "H" band is
assigned to a 2:1 reaction product of calcium and water.
Although higher order calcium cluster-water adducts were lightly discussed in the infrared study, the "H" band assignment is bolstered by the fact that it is red shifted from the Ca₂ \(^{1}P_u + ^{1}F_g\) transition and is easily photolyzed away with long wavelength light as was possible in the IR studies. The "F" band is relatively broad, perhaps indicative of a strong matrix interaction, whereas the "E", "D", and "C" bands are relatively sharp which is suggestive of discrete, bound states for the adduct.

Isotopic substitution studies were conducted with D₂O and H₂O\(^{18}\) hoping to better characterize the nature of the adduct bands. H₂O\(^{18}\) substitution was unsuccessful in shifting the adduct band structure; however, D₂O substitution generated relatively dramatic changes in the band structure red shifting the "C", "D", "E" bands and blue shifting the broad "F" band. The "C", "D", and "E" bands were red shifted by 90, 42, and 75 cm\(^{-1}\), respectively, and the "F" band was blue shifted by 143 cm\(^{-1}\). Attempts to associate these isotopic shifts in the band positions with vibronic progressions of an excited state in different normal modes were unsuccessful; therefore, these bands probably correspond to different electronic states of the metal-water adduct, different geometric isomers for the same 1:1 adduct, matrix site effects for the same electronic transition of the
adduct, or, in all probability, a composite of all these possibilities.

Selective photolysis of each of these adduct bands through a monochromator having a 20 Å bandpass was instrumental in establishing the interrelationship between these bands and distinguishing between their respective natures. Figure III-3 displays five traces corresponding to four, independent photolysis studies. Trace A' shows that selectively photolyzing the "F" band for 40 minutes was effective in eliminating the "C", "D", "E", and "F" bands equally with the concomitant generation of the "K", "J", and "L" product bands which suggests that all these bands correspond to different electronic transitions for the same adduct without site effects. However, trace B shows that a 30 minute selective photolysis of the "C" band was effective in totally eliminating the "C" band with only partial decreases in the intensities of the "D", "E", and "F" bands. This suggests that "C" may not be correlated with the "D" or "E" bands. Trace C shows that selectively photolyzing the "D" band for 30 minutes was effective in totally eliminating the "D" band with only partial decreases in the intensities of the "C", "E", and "F" bands which suggests that the "D" band can not be associated with the "E" or "C" bands. However, the structure of this "E" band is much narrower than the "E" band observed in the photolysis of the "C" band which suggests that both the
"D" and "C" bands correlate with the "E" band which is actually comprised of two superimposed bands. This may explain the anomalous intensity of the "E" band in trace A. Trace C' confirms the association between the "E" and "C" bands since this trace shows that a 15 minute photolysis of the "E" band is effective in eliminating both the "E" and "C" bands. Another photolysis study not depicted here shows that a 15 minute selective photolysis of band "E" after band "C" has been totally eliminated (trace B) is successful in totally destroying bands "F", "E", and "D" which supports the association of the "E" and "D" bands. In summary, photolysis of the "F" band suggests that it is equally associated with each of the other adduct bands, whereas selective photolysis of the "C", "D", and "E" bands suggests that the "C" and "D" bands are not associated, but each is associated with the "E" band which is probably composed of the two superimposed bands. Photolysis of each of these adduct bands was effective in generating the "J", "K", and "L" product bands. From this selective photolysis behavior it is possible to postulate that the adduct resides in two matrix sites or exists in two geometric forms and has three excited electronic states that are observed in the matrix. Two of the transitions are not significantly split by the site/isomer and correspond to bands "F" and "E" (however, band "E" is broadened in
one of the states), whereas the third transition is split by the site/isomer and corresponds to bands "D" and "C".

The infrared studies only report the formation of HCaOH from the photolysis of the Ca\ldots OH\textsubscript{2} adduct. Since the first excited states of HCaOH are probably quite high in energy, the low energy "J", "K", and "L" product bands probably originate from other photolysis products not identified in the infrared studies. Reasonable photolysis products include the diatomic CaO and the CaOH and the CaH radicals. CaO has two low energy electronic transitions around 11,549 cm\textsuperscript{-1} and 25,913 cm\textsuperscript{-1}; however, these energies do not correlate well with product bands observed in this study. The electronic structure of the CaOH radical should be quite similar to that of the CaF diatomic which has several low energy excited states at about 16,500 cm\textsuperscript{-1} (\textsuperscript{2}Π) and 18,850 cm\textsuperscript{-1} (\textsuperscript{2}Σ\textsuperscript{+}). These values correspond well with the assigned energies for the product bands observed in the matrix at 16,096 cm\textsuperscript{-1} and 18,126 cm\textsuperscript{-1}. Thus, in all probability, the CaOH radical is generated upon photolysis of the calcium-water adduct which extends a trend initially noted by Kauffman /7/ in that he observed SrOH and BaOH formation upon photolysis of their respective metal-water adducts, although he did not observe CaOH formation. Since H is homolytically cleaved during photolysis from the adduct in the formation of CaOH, it
is reasonable to believe that CaH would be formed by reaction of mobile H atoms and uncomplexed Ca atoms. The "L" product band at 15,727 cm\(^{-1}\) correlates well with the \(v_{\infty} = 15,755\) cm\(^{-1}\) \(B(2\Sigma^+) \rightarrow X(2\Sigma^+)\) transition for the CaH diatomic and hence is assigned accordingly. Therefore, this study reports the formation of both CaOH and CaH radicals as a consequence of selective photolysis of each of the calcium-water adduct bands.

3. STRONTIUM AND WATER

Cocondensation of strontium and water vapor on a sapphire substrate maintained at 15 K in an excess of krypton generates a transparent, yellow-brown matrix.

Figure III-4 shows an electronic absorption spectral trace corresponding to one experiment: Sr/H\(_2\)O/Kr. Figure III-5 shows six expanded scale absorption traces corresponding to the Sr/H\(_2\)O/Kr matrix being selectively photolyzed with different wavelengths of light dispersed by a monochromator. Table III-3 lists the assignments corresponding the band maxima for each of these spectra. The assignments are made after the matrix has been annealed to 42 K over a period of three minutes. The annealing process was not only effective in sharpening some of the bands (especially the \"E\" band: cf. Figures III-4 and III-5) with corresponding minor red and blue shifts in band positions but also resulted in an overall decrease in the
FIGURE III-4

ELECTRONIC ABSORPTION SPECTRUM FOR STRONTIUM AND WATER ISOLATED IN A KRYPTON MATRIX

Sr: H₂O:Kr = 1:98:3500
FIGURE III-5
EXPANDED SCALE ELECTRONIC ABSORPTION SPECTRA FOR STRONTIUM
AND WATER ISOLATED IN A KRYPTON MATRIX WITH
SELECTIVE PHOTOLYSIS

TRACE A - \( \text{Sr: } \text{H}_2\text{O: } \text{Kr} = 1:98:3500 \)

TRACE A' - Same as trace A but photolyzed for
15 minutes with light of \( \lambda = 6643 \text{ Å} \)
- 6663 Å

TRACE A" - Same as trace A' but photolyzed for
30 minutes with light of \( \lambda = 5716 \text{ Å} \)
- 5736 Å

TRACE B - Same as trace A but photolyzed for
30 minutes with light of \( \lambda = 5146 \text{ Å} \)
- 5166 Å

TRACE B' - Same as trace B but photolyzed for
15 minutes with light of \( \lambda = 5800 \text{ Å} \)
- 5820 Å

TRACE C - Same as trace A but photolyzed for
15 minutes with light of \( \lambda = 5416 \text{ Å} \)
- 5436 Å
TABLE III-3

ASSIGNMENTS FOR THE OPTICAL ABSORPTION SPECTRA
OF THE Sr/H₂O/Kr AND Sr/H₂O/Kr + hν SYSTEMS

<table>
<thead>
<tr>
<th>Peak</th>
<th>λ(Å)</th>
<th>ν(cm⁻¹)a</th>
<th>Species</th>
<th>Assignmente</th>
<th>Gas Phaseb (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4478</td>
<td>22 330</td>
<td>Sr</td>
<td>5s5p(1P)+5s2(1S)</td>
<td>21 698</td>
</tr>
<tr>
<td>A</td>
<td>4504</td>
<td>22 204</td>
<td>Sr</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>A</td>
<td>4618</td>
<td>21 654</td>
<td>Sr</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>B</td>
<td>4965</td>
<td>20 140</td>
<td>Sr</td>
<td>5s4d(3D)+5s2(1S)</td>
<td>20 150</td>
</tr>
<tr>
<td>B</td>
<td>5041</td>
<td>19 838</td>
<td>Sr</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>C</td>
<td>5177</td>
<td>19 318</td>
<td>Sr⋯⋯CH₂</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>D</td>
<td>5228</td>
<td>19 129</td>
<td>&quot;</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>E</td>
<td>5332</td>
<td>18 755</td>
<td>&quot;</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>F</td>
<td>5414</td>
<td>18 470</td>
<td>&quot;</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>G</td>
<td>5676</td>
<td>17 619</td>
<td>&quot;</td>
<td>A(1B₂)+X(1A₁)</td>
<td>?</td>
</tr>
<tr>
<td>H</td>
<td>5797</td>
<td>17 249</td>
<td>Sr⋯⋯(OH₂)₂</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>I</td>
<td>5917</td>
<td>16 901</td>
<td>Sr⋯⋯(OH₂)₂</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>J</td>
<td>6041</td>
<td>16 553</td>
<td>SrOH</td>
<td>2Σ⁺ + 2Σ⁺</td>
<td>?</td>
</tr>
<tr>
<td>K</td>
<td>6627</td>
<td>15 090</td>
<td>Sr⋯⋯(OH₂)₂</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>L</td>
<td>4121</td>
<td>24 268</td>
<td>Sr₂</td>
<td>1Πu +X(1Σ⁺)</td>
<td>24 600⁶</td>
</tr>
<tr>
<td>M</td>
<td>7003</td>
<td>14 279</td>
<td>SrH</td>
<td>2Σ⁺ +X(2Σ⁺)</td>
<td>14 352⁸</td>
</tr>
<tr>
<td>N</td>
<td>6768</td>
<td>14 777</td>
<td>SrOH</td>
<td>2Π+A(2Σ⁺)</td>
<td>?</td>
</tr>
<tr>
<td>N</td>
<td>6850</td>
<td>14 598</td>
<td>SrOH</td>
<td>2Π+A(2Σ⁺)</td>
<td>?</td>
</tr>
<tr>
<td>O</td>
<td>7310</td>
<td>13 680</td>
<td>Sr₂</td>
<td>1Σ⁺ +X(1Σ⁺)</td>
<td>13 224⁴</td>
</tr>
</tbody>
</table>

a Spectral coordinates in Å.
b Spectral coordinates in cm⁻¹.
e Labeled species consistent with observed transitions.
f Labeled species consistent with observed transitions.
TABLE III-3
(Continued)

<table>
<thead>
<tr>
<th>a</th>
<th>± 15 cm⁻¹.</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>From refs. 1, 11, and 16.</td>
</tr>
<tr>
<td>c</td>
<td>Band maximum in argon matrix.</td>
</tr>
<tr>
<td>d</td>
<td>$\nu_{oo}$ in krypton matrix.</td>
</tr>
<tr>
<td>e</td>
<td>Energies of transition are taken from band maxima unless noted otherwise.</td>
</tr>
<tr>
<td>f</td>
<td>Not shown in the spectra.</td>
</tr>
<tr>
<td>g</td>
<td>$\nu_{oo}$.</td>
</tr>
</tbody>
</table>
intensity of the "C", "D", "E", "F", and "G" bands with a concurrent increase in the intensity of the "H", "I", and "K" bands as can be seen from a comparison of Figures III-4 and III-5. High water dilution studies demonstrate that the "H", "I", and "K" bands are associated with higher order water interactions, \((H_2O)_n\) where \(n > 1\), since these bands are not apparent with water concentrations less than 150:1 for Kr: \(H_2O\) whereas the "C", "D", "E", "F", and "G" bands persist with the same relative magnitudes. Hence, annealing the matrix is evidently effective in allowing water to migrate through the matrix generating higher order water interactions.

The bands denoted by "A" and "B" in Figures III-4 and III-5 can be attributed to atomic resonance transitions for strontium since only these bands persist during the course of high strontium dilution experiments that exclude water doping. Previous absorption, emission, and MCD /15/ studies of strontium atoms in inert matrices are in good agreement with this spectra and have helped to establish the nature of the observed transitions corresponding to the "A" and "B" bands. From these studies, the bands denoted by "A" and "B" are assigned to the \(5s5p(^1P) + 5s^2(^1S)\) and the \(5s5d(^1D) + 5s^2(^1S)\) strontium atomic resonance transitions. The "A" band has triplet structure whereas the "B" band has a doublet character that becomes a blue shoulder with
water doping. The multiplet structures for these two transitions can probably be accounted for in terms of multiple site effects since the MCD studies \cite{15} demonstrate that the three distinct components observed in absorption for strontium in an argon matrix are generated by the Sr atom residing in three distinct matrix sites. Multiple sites for strontium in krypton probably reflects a poor fit for the atom in the lattice due to the atom's larger size. By analogy with Ca, the MCD study suggests that the three sites are of approximate $D_3h$ symmetry which would allow intensity borrowing from the $^1P + ^1S$ transition to the parity forbidden $^1D + ^1S$ transition. The bands denoted by "L" and "D" are correlated with electronic transitions of the strontium dimer since they are the first bands to grow in after the atomic bands, and their associated energies correlate well with electronic transitions for Sr$_2$ observed in previous matrix and gas phase studies \cite{1,15}. These studies allow one to assign the "O" band to the $^1\Sigma_u^+ + X(^1\Sigma_g^+)$ transition of Sr$_2$, and the "L" band to the $^1\Pi_u + X(^1\Sigma_g^+)$ transition. The MCD studies \cite{15} were instrumental in verifying the nature of the latter transition.

The bands denoted by "C", "D", "E", "F", and "G" in Figure III-5 may be correlated with the 1:1 reaction product of strontium and water since these bands are the
first bands to grow in as a consequence of having doped the matrix with water and maintain identical relative intensities with different water dilutions. The "H", "I", and "K" bands are associated with a 1:2 metal:water interaction since these bands are the second set of bands to grow in during the course of increasing the water concentration and increase in intensity during temperature cycling. In collaboration with the previous IR studies, the first set of bands may be associated with electronic transitions of the strontium-water adduct, Sr···OH₂. The "G" band is quite broad which may be indicative of a strong interaction with the matrix cage. In contrast, the "C", "D", "E", and "F" bands are relatively narrow which is suggestive of discrete, bound states for the adduct.

Isotopic substitution studies were conducted with D₂O and H₂O¹⁸ in lieu of H₂O¹⁶ in hopes of obtaining a better characterization for the adduct bands. H₂O¹⁸ substitution was uneventful in that no adduct bands shifted except for the "F" band which was slightly shifted to the red (30 cm⁻¹); however, D₂O substitution was effective in significantly red shifting most of the 1:1 adduct bands. The "C", "D", "E", "F", and "G" bands were red shifted by 17, 60, 92, 80, and 63 cm⁻¹, respectively. Attempts to rationalize these isotopic shifts in band position in terms of a vibronic progression of an excited state in different normal modes were unsuccessful. Therefore, as
was discussed for the calcium-water adduct, these bands probably correspond to a combination of different effects including multiple excited states, geometric isomers, and matrix site effects for the 1:1 Sr-H₂O complex.

Selective irradiation of each of these adduct bands through a monochromator was invaluable in establishing the interdependence of these bands which, in turn, was of assistance in understanding their respective natures. Figure III-5 shows six spectral traces corresponding to five independent photolysis experiments with light having a 20 Å bandpass. Trace A' shows that selectively photolyzing the "K" band for 15 minutes was effective in totally eliminating the "K", "I", and "H" bands without affecting any of the other bands which substantiates the previous association of these bands from water dilution and annealing studies. No product bands were generated from this photolysis which bears witness to the fact that these bands correspond to a different molecular species than the blue set of adduct bands since irradiation of these bands generated new product bands (vide infra). Trace A" shows that a subsequent 30 minute selective irradiation of the "G" band was successful in almost totally eliminating all the adduct bands ("G", "F", "E", "D", and "C") with a simultaneous generation of the "J", "M", and "N" product bands. Superficially, these results suggest that the five
adduct bands correspond to different electronic transitions for the same 1:1 adduct; however, further selective photolysis was illuminating. Trace B shows that a 30 minute irradiation of the "C" band was effective in totally eliminating the "C", "D", and "E" bands with only partial destruction of the "G" and "F" bands. This suggests that the "C", "D", and "E" bands are associated. Further photolysis (15 minutes) of this matrix hitting the "H" and unavoidably the "G" band is shown in trace B' and results in a significant decrease in the "G" and "F" bands which substantiates the association of these two bands. Trace C shows that a 15 minute selective photolysis of the "F" band is effective in totally eliminating the "F" band with only partial decreases in the intensities of the "G", "C", "D", and "E" bands which reinforces the independent nature of this band. Unfortunately, the "C", "D", and "E" bands are too closely positioned to allow a meaningful selective photolysis investigation of them. In summary, selective photolysis of the "G" band suggests a direct association of all the adduct bands; however, further selective photolysis of the other adduct bands indicates that the "G", "E", "D", and "C" bands and the "G" and "F" bands are associated. Photolysis of each of the 1:1 adduct bands was effective in generating the "J", "K", and "M" product bands. The selective photolysis behavior observed for the strontium-water system was not as conclusive as
the calcium-water system. In general, at least two electronic transitions are observed corresponding to the "G" and "F" bands and the "G" and "E", "D", and "C" bands. It is not possible from the information gleaned in this study to decipher the nature of the "E", "D", and "C" bands; however, it is likely that they arise from multiple sites and/or geometric isomers.

The infrared studies observed the generation of the HSrOH molecule and the SrOH radical from irradiation of the Sr⋯OH₂ adduct with light of λ = 520 - 580 nm. Subsequent photolysis of the HSrOH molecule with light of λ = 200 - 300 nm was successful in increasing the yield of the SrOH radical. In this study, selective photolysis of the Sr⋯OH₂ complex generated the "M", "N", and "J" bands which can probably be associated with the SrOH radical and the SrH diatomic by analogy with the observed photolysis products of the Ca-H₂O system. The electronic structure of the SrOH radical should be similar to that of the analogous SrF diatomic which has several low energy excited states at 17,264 cm⁻¹ (²Σ⁺) and 15,352 - 15,072 cm⁻¹ (²Π). Since SrOH was a photolysis product in the IR studies and these values correlate fairly well with the assigned energies for the product bands observed in the matrix at 16,553 cm⁻¹, 14,777 cm⁻¹, and 14,598 cm⁻¹, the "J" and "N" bands are tentatively assigned to the
\[ ^2\Sigma^+ + X(^2\Sigma^+) \] and the \[ ^2\Pi + X(^2\Sigma^+) \] transitions for SrOH, respectively. The 14,279 cm\(^{-1}\) "M" band correlates quite well with the 14,352 cm\(^{-1}\) \[ ^2\Sigma^+ + X(^2\Sigma^+) \] transition for CaH and hence is assigned accordingly. The lowest photodissociative excited states of HSR0H are evidently above 30,000 cm\(^{-1}\) since this energy of light was required to photodissociate this molecule. Although this region was studied, no product bands were observed which is consistent with the predissociative nature of these high energy states.

4. **BARIUM AND WATER**

Cocondensation of barium and water vapor on a sapphire substrate maintained at 15 K in an excess of krypton generates a transparent, colorless matrix.

Figure III-6 shows an electronic absorption trace corresponding to one experiment: Ba/D\(_2\)O/Kr. Figure III-7 shows two traces corresponding to expanded scale scans of two different isotopic experiments: Ba/D\(_2\)O/Kr and Ba/H\(_2\)O\(^{16}\)/Kr. Figure III-8 shows five absorption traces corresponding to the Ba/D\(_2\)O/Kr matrix being selectively photolyzed with different colors of light. Table III-4 lists the assignments corresponding to band maxima for each of these spectra. The assignments were made after having annealed the matrix to 42 K over a three minute period. This process was effective in decreasing the intensity
FIGURE III-6

ELECTRONIC ABSORPTION SPECTRUM FOR BARIUM AND WATER ISOLATED IN A KRYPTON MATRIX

$\text{Ba:D}_2\text{O:Kr} = 1:54:2750$
FIGURE III-7
EXPANDED SCALE ELECTRONIC ABSORPTION SPECTRA FOR BARIUM AND ISOTOPIC WATER ISOLATED IN A KRYPTON MATRIX

TRACE A  -  Ba:D₂O:Kr = 1:54:2750
TRACE B  -  Ba:HO¹⁶:Kr = 1:274:14,500
KRYPTON MATRIX

A - Ba + D_2O
B - Ba + H_2O^16

ABSORBANCE

CM^-1 (x 10^-3)

14.0
15.0
16.0
17.0
18.0
FIGURE III-8

ELECTRONIC ABSORPTION SPECTRA FOR BARIUM AND WATER ISOLATED IN A KRYPTON MATRIX WITH SELECTIVE PHOTOLYSIS

TRACE A1 - Ba:D₂O:Kr = 1:54:2750

TRACE A2 - Same as trace A1 but photolyzed for one minute and 45 sec with light of λ = 5901 Å - 5921 Å

TRACE A3 - Same as trace A2 but photolyzed for one minute and 45 sec with light of λ = 6463 Å - 6483 Å

TRACE A4 - Same as trace A3 but photolyzed for two minutes with light of λ = 6258 Å - 6278 Å

TRACE A5 - Same as trace A4 but photolyzed for one minute and 45 sec with light of λ = 6036 Å - 6056 Å
TABLE III-4

ASSIGNMENTS FOR THE OPTICAL ABSORPTION SPECTRA
OF THE Ba/H$_2$O/Kr AND THE Ba/H$_2$O/Kr + $h\nu$ SYSTEMS

<table>
<thead>
<tr>
<th>Peak</th>
<th>$\lambda$(Å)</th>
<th>$\tilde{\nu}$(cm$^{-1}$)$^a$</th>
<th>Species</th>
<th>Assignment$^c$</th>
<th>Gas Phase$^b$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3280</td>
<td>30 490</td>
<td>Ba</td>
<td>6s6d($^1$D) + 6s$^2$($^1$S)</td>
<td>30 237</td>
</tr>
<tr>
<td>B</td>
<td>5341</td>
<td>18 722</td>
<td>Ba</td>
<td>6s6p($^1$P) + 6s$^2$($^1$S)</td>
<td>18 060</td>
</tr>
<tr>
<td>B</td>
<td>5426</td>
<td>18 428</td>
<td>Ba</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>B</td>
<td>5474</td>
<td>18 269</td>
<td>Ba</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>C</td>
<td>5899</td>
<td>16 952</td>
<td>Ba$\cdots$OH$_2$ B($^1$B$_2$) + X($^1$A$_1$)</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>5961</td>
<td>16 775</td>
<td>&quot;</td>
<td>&quot;</td>
<td>?</td>
</tr>
<tr>
<td>D</td>
<td>6070</td>
<td>16 473</td>
<td>&quot;</td>
<td>&quot;</td>
<td>?</td>
</tr>
<tr>
<td>E</td>
<td>6152</td>
<td>16 255</td>
<td>&quot;</td>
<td>&quot;</td>
<td>?</td>
</tr>
<tr>
<td>F</td>
<td>6216</td>
<td>16 087</td>
<td>&quot;</td>
<td>&quot;</td>
<td>?</td>
</tr>
<tr>
<td>G</td>
<td>6431</td>
<td>15 550</td>
<td>&quot;</td>
<td>&quot;</td>
<td>?</td>
</tr>
<tr>
<td>G</td>
<td>6573</td>
<td>15 215</td>
<td>&quot;</td>
<td>&quot;</td>
<td>?</td>
</tr>
<tr>
<td>H</td>
<td>7083</td>
<td>14 118</td>
<td>&quot; A($^1$B$_1$) + X($^1$A$_1$)</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>7153</td>
<td>13 979</td>
<td>&quot;</td>
<td>&quot;</td>
<td>?</td>
</tr>
<tr>
<td>H</td>
<td>7229</td>
<td>13 833</td>
<td>&quot;</td>
<td>&quot;</td>
<td>?</td>
</tr>
<tr>
<td>I</td>
<td>7631</td>
<td>13 105</td>
<td>BaOH</td>
<td>$^2\Sigma^+ + X(^2\Sigma^+)$</td>
<td>?</td>
</tr>
<tr>
<td>J</td>
<td>8409</td>
<td>11 892</td>
<td>BaOH</td>
<td>$^2\Pi + X(^2\Sigma^+)$</td>
<td>?</td>
</tr>
<tr>
<td>K$^d$</td>
<td>7697</td>
<td>12 992</td>
<td>Ba$_2$</td>
<td>$^1\Sigma_u^+ + X(^1\Sigma_g^+)$</td>
<td>?</td>
</tr>
</tbody>
</table>

$^a$ ± 15 cm$^{-1}$.

$^b$ From refs. 1, 11, and 16.

$^c$ Energies of transition are taken from band maxima unless noted otherwise.

$^d$ Not shown in the spectra.
of the "F" band while increasing the intensity of the "G" band. Also, the triplet structure of the "H" band and the red shoulder on the "C" band were partially washed out. The bands which were discriminated against in the temperature cycling process probably correspond to unstable matrix site effects.

The bands denoted by "A" and "B" in Figure III-6 can be attributed to atomic resonance transitions for barium since only these bands persist during the course of high Ba dilution experiments without water doping. Comparison of these bands' energy positions with gas phase transition energies /11/ allows the probable assignment of the "A" and "B" bands to the $6s6d(^1D) + 6s^2(^1S)$ and the $6s6p(^1P) + 6s^2(^1S)$ atomic resonance transitions for barium. The "A" band is blue shifted (253 cm$^{-1}$) relative to the gas phase transition, as is typical according to relatively strong repulsive matrix cage interactions, and is quite weak and broad compared to the "B" band. The weak character of this band is consistent with the parity-forbidden nature of the transition from which it originates. Matrix site symmetry was effective in allaying the forbidden character of the low energy $^1D + ^1S$ transitions of calcium and strontium in argon and krypton matrices; consequently, it is quite conceivable that the same static symmetry mechanism plays an important role in breaking down the selection rules for barium's high energy
\[ ^1D + ^1S \] transition even though the transitions arise from different electron configuration rearrangements. It was not possible to learn whether or not the low energy \[ 6s5d(^1D) + 6s^2(^1S) \] transition for Ba had also partially shed its forbidden character by virtue of matrix site symmetry as was noted for Ca and Sr, since this near-infrared transition is just barely beyond the low energy range where the U.V.-VIS spectrometer can reliably probe. The major "B" band is blue shifted by 209 cm\(^{-1}\) relative to the gas phase transition and has triplet structure with a red shoulder. The triplet structure may possibly be interpreted in the same manner as was discussed for the band structure of magnesium. The red shoulder is probably caused by the Ba atom residing in a different matrix site since its large size generates a poor fit in the rare gas lattice.

The structureless band denoted by "K" is assigned to an electronic transition of the barium van der Waals dimer since this is the first band to grow in after the atomic bands upon increasing the Ba concentration, and the growth displays a quadratic dependence on the metal deposition rate. Only one other study of barium systems has been reported /10/ but the results are largely inconclusive due to Sr and Mg impurities and failure to isolate Ba sufficiently to be able to discriminate against higher order metal aggregates. Four unstructured absorptions
in argon to the red of atomic features at 570 nm, 600 nm, 735 nm, and 850 nm were reported. They point out that from the trend in Mg$_2$, Ca$_2$, and Sr$_2$ absorptions and the intermediate positions of the IIA mixed metal diatomics, the $1\Sigma_u^+(1S + 1P) + 1\Sigma_g^+(1S + 1S)$ absorption for Ba$_2$ is predicted to be around 760 nm which is in very good agreement with the 7697 Å "K" band for Ba$_2$ in a krypton matrix reported in this study. Although the previous study could not eliminate the possibility that the 735-753 nm band could be assigned to an atomic $3P + 1S$ transition, concentration studies in this work establish that the "K" band arises from Ba$_2$ and hence may tentatively be assigned to the $1\Sigma_u^+ \leftrightarrow 1\Sigma_g^+$ transition. Assuming this assignment is correct, a lower limit to the dissociation energy for the excited state separating to $1P$ and $1S$ atoms may be estimated from

$$D'_o = E(1P + 1S) - E_{oo} + D''_o.$$ 

$D'_o$ calculates to be approximately 7,400 cm$^{-1}$ assuming $D''_o = 1600$ cm$^{-1}$ /10/ and $E_{oo} = 12,250$ from the red cutoff of the "K" band observed in absorption.

The bands denoted by "C", "D", "E", "F", "G", and "H" in Figure III-6 may be associated with the 1:1 reaction product of barium and water since these bands grow in as a consequence of having doped the matrix with water and
maintain identical relative intensities with different water dilutions. In collaboration with the previous IR studies /7/, these bands may be identified with the barium-water adduct, Ba···OH₂. The "C", "D", "E", and "G" bands are clustered together to the red of the atomic transition and have relatively narrow bandwidths whereas the "H" band is red shifted considerably from this cluster of bands and has a broad, triplet structure.

Isotopic substitution studies were conducted with D₂O and H₂O₁₈ in lieu of H₂O₁₆ in hopes of deriving a better characterization of the nature of the adduct bands. H₂O₁₈ substitution was uneventful in that none of the adduct bands significantly shifted or changed in intensity; however, D₂O substitution effected a number of changes in the band structure as is depicted in Figure III-7. First, the intensities of the "F" and "D" bands enhanced dramatically upon D₂O substitution with associated shifts of 163 cm⁻¹ to the red and 73 cm⁻¹ to the blue, respectively. Second, substitution was also effective in eliminating the red shoulder on the major "C" band with a simultaneous resolution of a blue shoulder. Finally, the "C", "E", and "G" bands were also red shifted by 34 cm⁻¹, 126 cm⁻¹, and 62 cm⁻¹, respectively. The "H" bands were not affected by isotopic substitution. Attempts to interpret these isotopic shifts in band position in terms of a vibronic progression of
an excited state in different normal modes were unsuccessful; consequently, these bands probably correspond to a combination of multiple excited states, geometric isomers, and matrix site effects for the 1:1 Ba-H₂O complex.

Selective irradiation of each of these adduct bands through a monochromator was of assistance in understanding their interrelationships and their respective natures. Figure III-8 shows five spectral traces corresponding to four photolysis experiments with different colored light. Trace A2 shows that a one minute and 45 second selective photolysis of the "C" band effected about a 50% decrease in the intensity of the "C" band without affecting the other bands except, perhaps, the "D" band which rides on the red shoulder of the "C" band and the "H" band which decreased in intensity. This suggests that the "D" band is only associated with the "H" band. Trace A3 shows that a one minute and 45 second photolysis of the "G" band decreases the intensity of the "G" band by over 50% without affecting the intensities of the other bands except the "H" band that again decreases slightly in intensity. This suggests an association of the "G" band with the "H" band also. Similar behavior is observed for the "F", "E", and "D" bands so that one may summarize the overall photolysis behavior by stating that the "C", "D", "E", "F", and "G" bands are all independent of each other, but all of these bands are associated with
the "H" band. This statement is not rigorous with regard to the "F" and "E" bands since it is not possible to distinguish between them photolytically. In another experiment not shown, photolysis of the "H" band was discovered to be effective in eliminating all of the adduct bands which bolsters the correlation of the "H" band with all of the other bands. Photolysis of each of the adduct bands was proficient in generating both the "I" and "J" product bands. The photolytic behavior of the adduct bands suggests the presence of two electronic states for the adduct corresponding to the "H" band and the "C", "D", "E", "F", and "G" band cluster. This band cluster may correspond to an electronic state split by geometric isomers or matrix sites.

The infrared investigations of the barium-water chemistry /7/ reported the generation of the HBaOH molecule and the BaOH radical from irradiation of the Ba···OH$_2$ complex with light of $\lambda = 580$-620 nm. Only subsequent photolysis of HBaOH with light of $\lambda = 200$-300 nm was successful in increasing the yield of the BaOH radical. In this study, selective photolysis of the Ba···OH$_2$ complex generated the "I" and "J" product bands which are probably only associated with the BaOH and BaH products (as was observed for the calcium- and strontium-water systems) since the HBaOH product probably has electronic states beyond the range and sensitivity of the spectrometer. The analogous BaF molecule
has two low energy electronic states at 11,547 cm\(^{-1}\) - 12,278 cm\(^{-1}\) (\(2\Pi\)) and 14,063 cm\(^{-1}\) (\(2\Sigma^+\)). The BaH molecule has electronic states at 15,055 cm\(^{-1}\) - 14,605 cm\(^{-1}\) (\(2\Pi\)) and 11,092 cm\(^{-1}\) (\(2\Sigma^+\)). The "I" and "J" bands occur at 13,105 cm\(^{-1}\) and 11,892 cm\(^{-1}\), respectively, and probably can not be correlated to the transitions for BaH since the shifts that would be required to make a correspondence are too large in magnitude to be reasonable. Since only the \(2\Sigma^+ - 2\Sigma^+\) system was observed in absorption for CaH and SrH in this study, it is quite reasonable that BaH was being formed but just couldn't be observed since the potentially perspicuous \(2\Sigma^+ - 2\Sigma^+\) transition for BaH is probably less than 11,000 cm\(^{-1}\) which is beyond the range of the spectrometer. Therefore, by elimination, the "I" and "J" bands are tentatively assigned to the \(2\Sigma^+ - 2\Sigma^+\) and the \(2\Pi^+ - 2\Sigma^+\) transitions for the BaOH radical, respectively. Both the \(2\Pi\) and \(2\Sigma^+\) excited states were observed for the CaOH and SrOH radicals.

D. DISCUSSION

1. NATURE OF THE ELECTRONIC STATES OF THE GROUP IIA METAL-WATER COMPLEX

   a. PRELIMINARY CONSIDERATIONS

Mg, Ca, Sr, and Ba metal atoms initially form a complex with water such that the metal is coordinated to the 3a\(_1\) lone electron pair on the oxygen atom of the water molecule. Calculations for Mg indicate /9/ that the metal
is symmetrically coordinated in the plane of the water molecule according to the $C_{2v}$ point group. Hydrate or adduct formation perturbs the electronic structure of the metal atom in such a manner that the $1^p + 1^s$ and the $1^D + 1^s$ atomic transitions are apparently split into several states by the interaction and red shifted from their respective uncomplexed resonance transitions. Selective photolysis studies were fruitful in establishing the interrelationships of the sets of multiple bands generated upon adduct formation. Insight to the nature of the perturbation that leads to red shifted spectra may be gleaned from an examination of Figure III-9 which depicts the metal in its ground and excited states approaching the $3a_1$ lone pair orbital of water from infinite separation. At suitable metal-water separations, the metal is unperturbed by the water interaction, and a normal atomic transition is observed which is of energy $E_2$ in the diagram. As the metal approaches the water molecule in closer proximity, an attractive interaction is encountered such that the eventual equilibrium arrangement finds the metal-water complex bound in a potential energy well. For reasons which will be developed later, the water is more highly attracted to the metal in its excited state than its ground state so that $\epsilon^* > \epsilon$ which implies that $E_2 > E_1$. Consequently, the A + X metal-water complex transition is red shifted
FIGURE III-9

SCHEMATIC DIAGRAM OF THE POTENTIAL ENERGY SURFACES FOR THE METAL–WATER INTERACTION WITH THE METAL IN ITS GROUND AND EXCITED STATES
\[ \epsilon^* \gtrsim \epsilon \]
\[ E_2 \gtrsim E_1 \]
\[ (M\ldots OH_2)^* \]
\[ \text{atomic transition} \]
\[ R \]
\[ (M\ldots OH_2) \]

\[ E_1 \]
\[ E_2 \]

\[ X \rightarrow A \]

\[ \text{ENERGY} \]
relative to the atomic lines. Since the ground state interaction with water, $\varepsilon$, is very weak for the Group IIA metals, the difference between $E_1$ and $E_2$ is a measure of the minimum dissociation energy of the exciplex in its bound excited state, $\varepsilon^\ast$, dissociating to $M^\ast (^1D$ or $^1P) + H_2O(^1A_1)$. More precisely,

$$D'_0 = E(^1D \text{ or } ^1P + ^1S) - E_{oo} + D''_0$$

where $E_{oo}$ may be estimated from the red cutoff of the adduct bands observed in absorption for a particular state, and $D''_0$ may be evaluated from previous calculations /9/. The $D'_0$ values for the metal-water complexes in different electronic states are tabulated in Table III-5.

The Group IIA metal-water complex has an unequivocal electronic ground state of $^1A_1$ since the s orbital is non-degenerate under any symmetry resolution. However, the metal-water complex potentially has eight low energy excited states corresponding to the water interaction splitting the p orbital and d orbital degeneracy of the metal atom in the $C_{2v}$ point group. Splitting of both the p and d orbitals is possible for the heavier Group IIA metals since they have closely spaced, low energy $^1P$ and $^1D$ atomic states which can be perturbed by interaction with water. There are three electronic states generated by perturbation of the p orbital by water which are labeled
## TABLE III-5

DISSOCIATION ENERGY ESTIMATES\(^a\) FOR THE GROUP IIA
METAL-WATER COMPLEXES, EXCITED STATES IN SOLID KRYPTON

<table>
<thead>
<tr>
<th>Molecule</th>
<th>State</th>
<th>(lp1s)</th>
<th>(1Dp1s)</th>
<th>(0^{-})</th>
<th>(D_p)</th>
<th>(D_p')</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg···OH(_2)</td>
<td>(^1\text{B}_2)(^f)</td>
<td>35 032</td>
<td>—</td>
<td>27 380</td>
<td>7 652 + (D_0'')</td>
<td>8 457</td>
</tr>
<tr>
<td>Ca···OH(_2)</td>
<td>(^1\text{B}_2)(^g)</td>
<td>—</td>
<td>21 825</td>
<td>18 135</td>
<td>3 691 + (D_0'')</td>
<td>6 211</td>
</tr>
<tr>
<td>&quot;</td>
<td>(^1\text{A}_1)</td>
<td>—</td>
<td>—</td>
<td>19 810</td>
<td>2 016 + (D_0'')</td>
<td>4 536</td>
</tr>
<tr>
<td>&quot;(&quot;D&quot;)</td>
<td>(^1\text{B}_1)(^g)</td>
<td>—</td>
<td>—</td>
<td>20 650</td>
<td>1 176 + (D_0'')</td>
<td>3 696</td>
</tr>
<tr>
<td>&quot;(&quot;C&quot;)</td>
<td>(^1\text{B}_1)(^g)</td>
<td>—</td>
<td>—</td>
<td>21 115</td>
<td>711 + (D_0'')</td>
<td>3 231</td>
</tr>
<tr>
<td>Sr···OH(_2)</td>
<td>(^1\text{B}_2)(^g)</td>
<td>—</td>
<td>19 838</td>
<td>16 790</td>
<td>3 048 + (D_0'')</td>
<td>—</td>
</tr>
<tr>
<td>Ba···OH(_2)</td>
<td>(^1\text{B}_2)</td>
<td>18 269</td>
<td>—</td>
<td>13 436</td>
<td>4 833 + (D_0'')</td>
<td>—</td>
</tr>
<tr>
<td>&quot;(&quot;G&quot;)</td>
<td>(^1\text{B}_1)</td>
<td>&quot;</td>
<td>—</td>
<td>15 300</td>
<td>2 970 + (D_0'')</td>
<td>—</td>
</tr>
<tr>
<td>&quot;(&quot;C&quot;)</td>
<td>&quot;</td>
<td>&quot;</td>
<td>—</td>
<td>16 775</td>
<td>1 494 + (D_0'')</td>
<td>—</td>
</tr>
</tbody>
</table>

\(^a\) For \((\text{M}···\text{OH}_2)^*\) dissociating to \(\text{M}^* + \text{H}_2\text{O}(^{1}\text{A}_1)\).

\(^b\) \(\text{cm}^{-1}\).

\(^c\) Estimated from red cutoff of absorption band.

\(^d\) \(D_0''\) values for Mg···OH\(_2\) and Ca···OH\(_2\) of 805 \(\text{cm}^{-1}\) and 2520 \(\text{cm}^{-1}\), respectively.

\(^e\) For multiple bands, energy values are taken from the major band position.

\(^f\) \(^1\text{B}_2\) is the logical choice since it is the strongest bound state for the Ca-, Sr-, and Ba-H\(_2\)O complexes.

\(^g\) Assumes adiabatic correlation to \(\text{M}^*(^{1}\text{D})\) from an avoided surface intersection.
$^1B_2$, $^1B_1$, and $^1A_1$, corresponding to the promoted electron residing in the $b_2$-$p_y$, $b_1$-$p_x$, and the $a_1$-$p_z$ orbitals, respectively. Reference to Figure III-10 is helpful in understanding the nature of these excited states. From this figure, it is apparent that occupation of the $a_1$-$p_z$ orbital by the promoted electron directs electron density toward the $3a_1$ lone electron pair on water which suggests that the $^1A_1$ state is a repulsive state due to electron repulsion. Both the $^1B_2$ and $^1B_1$ states are expected to be attractive since these states correspond to an orbital occupancy that disperses the electron density away from the nucleus so the $3a_1$ lone pair on water may achieve an enhanced Coulombic attraction with the metal's nucleus. _Ab initio_ studies (see Table I-1) for the (Li$\cdots$OH$_2$)$^+$ adduct report that the $^2A_1$ state is repulsive whereas the $^1B_2$ and $^1B_1$ states are attractive. These calculations also indicate that the $^1B_2$ state is more stable than the $^1B_1$ state because occupation of the $b_2$-$p_y$ orbital allows for a favorable quadrupole-quadrupole interaction with the water's in-plane H-O-H quadrupole along the $y$-axis whereas occupation of the $b_1$-$p_x$ orbital of the metal generates a repulsive quadrupole-quadrupole interaction with the filled, out-of-plane, non-bonding $b_1$ orbital of water. For the lithium-water interaction, the calculated energy difference between the $^1B_2$ and the $^1B_1$ excited states is 4.3 kcal/mole.
FIGURE III-10

SCHEMATIC DIAGRAM SHOWING THE SYMMETRY DISPOSITION OF THE WATER MOLECULE IN A CARTESIAN COORDINATE SYSTEM
There are five electronic states generated through perturbation of the metal d-orbitals by water, splitting the fivefold degeneracy in the C\textsubscript{2v} point group. These states are labeled $^1A_\text{1}(z^2)$, $^1A_\text{1}(x^2-y^2)$, $A_\text{2}$, $B_\text{1}$, and $B_\text{2}$ and correspond to the promoted electron residing in the $a_\text{1}-d_{z^2}$, the $a_\text{1}-d_{x^2-y^2}$, the $a_\text{2}-d_{xy}$, the $b_\text{1}-d_{xz}$, and the $b_\text{2}-d_{yz}$ orbitals, respectively. However, in view of what has been learned regarding the stabilities of the $^1A_\text{1}$, $^1B_\text{1}$, and $^1B_\text{2}$ states related to p orbital occupancy, there is strong reason to believe that a number of these states which arise from d orbital occupancy are also repulsive in nature. Again, reference to Figure III-10 is of pedagogic value. Certainly, the $^1A_\text{1}(z^2)$ state is repulsive since it corresponds to $a_\text{1}-d_{z^2}$ orbital occupancy that directs electron density toward the $3a_\text{1}$ lone electron pair on water as was true for the $a_\text{1}-p_{z}$ orbital. The $^1B_\text{1}$ state is also predictably unstable since it corresponds to $b_\text{1}-d_{xy}$ orbital occupancy. Although this occupancy disperses electron density away from the nucleus core of the metal, it does so by directing the charge density toward the $b_\text{1}$ lone pair on water inducing electron repulsion again. The $^1B_\text{2}$ state is also expected to be unstable since the corresponding $b_\text{2}-d_{yz}$ orbital occupancy places charge density, in-plane, indirectly toward the $3a_\text{1}$ lone pair. However, the $A_\text{1}(x^2-y^2)$ and the $A_\text{2}$ states are probably relatively stable since they correspond to $a_\text{1}-d_{x^2-y^2}$ and $a_\text{2}-d_{xy}$ orbital
occupancies directing charge density away from the metal in such a manner as to avoid overlap with the electron density on the water molecule. The energy of the $^1A_1$ state is probably degenerate with the $^1A_2$ state since they have equally favorable and repulsive quadrupole-quadrupole components with the water's in-plane and out-of-plane quadrupoles. Although the $^1A_2$ state is probably stable, it can not be observed in absorption if $C_{2v}$ symmetry is sustained since a $^1A_2 + ^1A_1$ electron transition is electric-dipole forbidden. In summary, for a Group IIA metal-water interaction, there exists an unequivocal $^1A_1$ ground state arising from the $^1S + ^1A_1$ combination; however, there are three bound excited states that can be accessed from the $^1A_1$ ground state which are derived from $^1F + ^1A_1$ and $^1D + ^1A_1$ combinations, specifically: $^1B_2$, $^1B_1$, and $^1A_1$. Therefore, the multiple set of absorption bands generated upon adduct formation should, at least in part, correlate to these three electronic states which arise from symmetry splitting of p and d orbital degeneracy.

In studying the interaction of the metal-water complex, Bentley /8/ states that the principal noncovalent attractive force between the metal and water is electrostatic in origin with minor polarization and charge transfer components. Electrostatic attraction should increase dramatically by electronic excitation of the adduct since electron promotion
involves charge density dispersal from the vicinity of the metal nucleus by vacating a $a_1$-s orbital. This generates a $\sigma$ hole in the molecular orbital structure of the metal that makes it more electropositive to the $3a_1$ electron pair on water. The ground state of the Group IIA metal-water complex is calculated to be very weakly bound, i.e., primarily van der Waals attraction. Therefore, adduct electronic transitions should be accompanied by significant increases in the bonding interactions and decreases in the internuclear $M$-$O$ bond distances which, in turn, implies large off-diagonal Franck-Condon factors for the transition. These factors may play an important role in the photo-induced reactions of the metal-water complex as will be discussed shortly.

b. MAGNESIUM AND WATER

The magnesium-water adduct band has no evident band structure; rather, it displays a rather broad continuous absorption encompassing a $4,500 \text{ cm}^{-1}$ range. This broadness should be anticipated from the van der Waals nature of bonding between Mg and H$_2$O in that continuous absorption spectra are characteristic of molecular species that are very weakly bound in the ground state but have a well defined potential energy minima in the excited state. This is the case since absorption may take place from a wide, continuous range of internuclear separations in the weakly
bound ground state which along the excited state potential energy surface corresponds to a wide, continuous range of energies that is reflected in a broad, continuous absorption band. For this reason as well, it would be difficult to detect the presence of several closely spaced, bound excited states in absorption from the ground state of a molecular species with a poorly defined internuclear separation. However, it is also possible to generate continuous spectra by absorption into a dissociative excited state. The first excited state potential energy surfaces for the HMGOH species are probably in the UV which states may be able to correlate with the excited state of the adduct at about 30,000 cm$^{-1}$ since the insertion reaction is exothermic by about 7,500 cm$^{-1}$ (see Table III-6). Thus, the excited states of the adduct may be unbound with respect to rearrangement to form the insertion product in an excited state in which case continuous spectra would be observed in absorption. Although from preliminary considerations several adduct excited states might be expected to be apparent in electronic absorption studies, these excited states are probably washed out by the observed broad absorption continuum.

c. **CALCIUM AND WATER**

Band intensity behavior observed during selective photolysis studies of the Ca$\cdot\cdot\cdot$OH$_2$ adduct bands suggest that
### TABLE III-6

ESTIMATED HEATS OF REACTION\(^{a,b}\) \((\text{kcal/mole})\)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\Delta H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Mg} + \text{H}_2\text{O} \rightarrow \text{HMgOH})</td>
<td>-22 (\pm) 10</td>
</tr>
<tr>
<td>(\text{Mg} + \text{H}_2\text{O} \rightarrow \text{MgOH} + \text{H})</td>
<td>+21 (\pm) 5</td>
</tr>
<tr>
<td>(\text{HMgOH} \rightarrow \text{MgOH} + \text{H})</td>
<td>+43 (\pm) 10</td>
</tr>
<tr>
<td>(\text{Ca} + \text{H}_2\text{O} \rightarrow \text{HCaOH})</td>
<td>-27 (\pm) 10</td>
</tr>
<tr>
<td>(\text{Ca} + \text{H}_2\text{O} \rightarrow \text{CaOH} + \text{H})</td>
<td>+14 (\pm) 5</td>
</tr>
<tr>
<td>(\text{HCaOH} \rightarrow \text{CaOH} + \text{H})</td>
<td>+41 (\pm) 10</td>
</tr>
<tr>
<td>(\text{Sr} + \text{H}_2\text{O} \rightarrow \text{HSrOH})</td>
<td>-23 (\pm) 10</td>
</tr>
<tr>
<td>(\text{Sr} + \text{H}_2\text{O} \rightarrow \text{SrOH} + \text{H})</td>
<td>+15 (\pm) 5</td>
</tr>
<tr>
<td>(\text{HSrOH} \rightarrow \text{SrOH} + \text{H})</td>
<td>+38 (\pm) 10</td>
</tr>
<tr>
<td>(\text{Ba} + \text{H}_2\text{O} \rightarrow \text{HBarOH})</td>
<td>-41 (\pm) 10</td>
</tr>
<tr>
<td>(\text{Ba} + \text{H}_2\text{O} \rightarrow \text{BaOH} + \text{H})</td>
<td>+4 (\pm) 5</td>
</tr>
<tr>
<td>(\text{HBarOH} \rightarrow \text{BaOH} + \text{H})</td>
<td>+45 (\pm) 10</td>
</tr>
</tbody>
</table>

\(^{a}\) Heats of reaction were estimated using bond energy data from references 16, 19 and 20.

\(^{b}\) Group IA metal hydride dissociation energies were used for the H-MOH bond energies.
the adduct should have three stable excited electronic states, $^1B_2$, $^1B_1$, and $^1A_1$, which should be correlated to the three matrix transitions. From previous arguments that are corroborated by quantum-chemical calculations, the $^1B_2$ state should be lower in energy relative to the $^1B_1$ state both of which are diabatically derived from a splitting of the p orbital degeneracy. Adiabatically, however, the $^1B_1$ and the $^1B_2$ surfaces correlate into the $M(^1D) + H_2O(^1A_1)$ combination since these bound surfaces have an avoided intersection with the $^1B_1$ and $^1B_2$ surfaces that arise from breaking the d orbital degeneracy. The $^1A_1$ surface has no surface crossings and hence correlates directly into the $M(^1D) + H_2O(^1A_1)$ combination. The $^1B_2$ state can not be assigned to the "C" and "D" bands since this implies that the $^1B_2$ state is less stable than the $^1B_1$ state. The $^1B_2$ state is more appropriately assigned to the "F" band since such an association allows for a reasonable energy separation between the $^1B_2$ and $^1B_1$ states that is not achievable otherwise. From the barium-water discussion to be developed shortly, it is apparent that the $^1B_1$ state is heavily influenced by slightly different geometric conformations for the adduct which generate splittings of this state; therefore, the "C" and "D" bands are both tentatively assigned to the $^1B_1$ state split by two geometric isomers of the adduct with the "C" band corresponding to the most stable $^1B_1$ state. By elimination, the $^1A_1$ state is tenta-
tively assigned to the "E" band. Different geometric conformations of the adduct that would split the $^1B_1$ state yet leave the $^1B_2$ state unperturbed correspond to the metal tilting out of the plane defined by the water molecule breaking the $C_{2v}$ symmetry and giving $C_s$ symmetry so the "C" band may more appropriately correspond to an $A'$ state. Quantum-chemical calculations by Curtiss and Frurip /9/ indicate that this conformation is the most stable for the Be-H$_2$O adduct, but very little energy is required to place the metal atom back in-plane. For the ground state of the adduct, stable tilted conformations are reasonable since, with this geometry, more significant ligand → metal $\pi$ bonding may be achieved by a mixing of the filled $b_1$-a" orbital of water with an unfilled metal orbital of $b_1$-a" symmetry. The fact that a definite band structure is observed for the Ca···OH$_2$ adduct as opposed to the Mg···OH$_2$ adduct suggests that the ground state has a relatively well defined potential energy minimum, the lack of which was probably partially responsible for washing out discrete band structure for the Mg···OH$_2$ adduct. In summary, the "F", "E", and "D" and "C" bands are tentatively assigned to $^1B_2 + ^1A_1$, $^1B_1 + ^1A_1$, and $^1A_1 + ^1A_1$ transitions for the adduct, respectively, where the $^1B_1 + ^1A_1$ transition is believed to be split by the presence of two geometric isomers for the adduct, the existence of which will be
shortly substantiated in the discussion of the band
structure for the \( \text{Ba} \cdots \text{OH}_2 \) adduct.

Isotopic substitution generated various red and blue
shifts in the electronic absorption band positions for the
calcium-water complex which may be rationalized, in a
general manner, in the context of isotopic frequency shifts
for several vibrational modes of the adduct. The \( \Gamma \)-shaped
adduct (\( C_{2v} \) point group) has six nondegenerate vibrations,
five of which are in the plane of the adduct molecule;
however, only three of these vibrations are expected to
have both a difference in their vibrational frequency for
the ground and the excited state and display a deuterium
isotope shift. These three vibrations correspond to three
bending modes: (1) the \( A_\perp \) bending mode primarily composed
of the bending mode of water; (2) the \( E_2 \) bending mode which
corresponds to an in-plane wagging motion of the water
molecule with respect to calcium atom; and (3) the \( E_1 \) bending
mode that can be identified with an out-of-plane rocking
motion of the water molecule with respect to the calcium
atom. There is strong reason to believe that the \( A_\perp \) bending
mode of water should be significantly different in the
ground as opposed to the excited state of the adduct.
Adduct formation in the infrared studies \(^7\) was evidenced
by a decrease in the bending mode frequency of water. This
decrease was postulated to have been induced by a partial
charge transfer from the $3a_1$ orbital of water (which is the orbital accounting for the bent configuration of water) to the metal atom due to a Coulombic attraction of the metal nucleus. As per previous discussions, electronic excitation to attractive states of the adduct disperses charge from the vicinity of the metal nucleus to enhance the Coulombic forces of attraction thereby increasing the partial electron transfer from the $3a_1$ orbital to the metal with a concomitant further decrease in the $A_1$ bending mode of water. The vibrational frequencies of both the $B_2$ and $B_1$ bending modes should increase significantly in going from the ground to the excited state since the Ca-O bond strength increases dramatically for this same transition according to previous arguments. In review, the vibrational frequency of the $A_1$ mode should be lower in the excited state relative to the ground state whereas the $B_1$ and $B_2$ frequencies should be higher; therefore, for the $A_1$ mode, deuterium substitution should induce blue shifts in a 0-0 transition, whereas, considering only the $B_1$ or $B_2$ modes, deuterium substitution should cause red shifts in a 0-0 transition. Of course, the actual overall blue or red shifts observed in the absorption band positions correspond to a composite of these three effects where a blue shift indicates that the $A_1$ vibrational frequency change dominates over the $B_2$ and the $B_1$ frequency changes, and a red shift indicates the $B_2$ and the $B_1$
frequency changes are predominant. With this in mind, it is evident that the $^1B_2 + ^1A_1$ electronic transition corresponding to the "F" band of the adduct, which was blue shifted upon deuterium substitution, causes a dominating change in the bending mode of water, whereas the $^1A_1 + ^1A_1$ and the $^1B_1 + ^1A_1$ transitions corresponding to the "C", "D", and "E" bands, which were red shifted upon substitution, do not.

Table III-5 lists dissociation energy estimates for several excited states of the Ca$\cdots$OH$_2$ adduct in solid krypton. Assuming the dissociation energy of the ground state is 2,520 cm$^{-1}$/17/, the $^1B_2$, $^1A_1$, and $^1B_1$ states are bound by 6,211 cm$^{-1}$, 4,536 cm$^{-1}$, and 3,696 cm$^{-1}$ (for the most stable $^1B_1$ state), respectively. The dissociation energies for the $^1B_2$ and the $^1B_1$ states are calculated relative to the $^1D + ^1S$ transition since, although these states diabatically arise from the $M^*(^1P) + H_2O(^1A_1)$ combination, they encounter an avoided surface crossing with the $^1B_2$ and the $^1B_1$ states arising from the $M^*(^1D) + H_2O(^1A_1)$ combination. The $^1B_2$ and $^1B_1$ states arising from this latter combination are not expected to be stable so the predictably bound $^1B_2$ and $^1B_1$ states arising from the former combination are probably destabilized by the avoided crossing. These dissociation energies are in good qualitative
agreement with a number of quantum-chemical studies that have reported dissociation energies for metal-water complexes in their excited and ground states. The results of these calculations are summarized in Table I-1. For example, the calculated dissociation energy of \((\text{Be}\cdots\text{OH}_2)^*\) in the \(3\text{B}_2\) excited state is 18.6 kcal/mole which compares well with the 17.8 kcal/mole value for the \(1\text{B}_2\) state of \((\text{Ca}\cdots\text{OH}_2)^*\). These calculations also indicate there is a 1,500 cm\(^{-1}\) and a 1,855 cm\(^{-1}\) energy spacing between the \(2\text{B}_2\) and the \(2\text{B}_1\) states for \((\text{Li}\cdots\text{OH}_2)^*\) and \(\text{Al}\cdots\text{OH}_2\), respectively. These values are in good agreement with the 1,675 cm\(^{-1}\) spacing observed between the \(1\text{B}_2\) and \(1\text{B}_1\) states of \((\text{Ca}\cdots\text{OH}_2)^*\). \textit{Ab initio} calculations have not considered the \(1\text{A}_1\) state arising from the \(1\text{D} + 1\text{A}_1\) combination for the Group II A metals.

d. STRONTIUM AND WATER

Band intensity behavior observed during selective photolysis studies of the \(\text{Sr}\cdots\text{OH}_2\) adduct was not as informative as the behavior observed in the \(\text{Ca}-\text{H}_2\text{O}\) system but suggested that at least two excited electronic states exist. The relative position and the photolysis behavior of the "G" band is identical to that displayed by the "F" band for the \(\text{Ca}\cdots\text{OH}_2\) adduct. Photolysis of the "G" band was successful in eliminating all of the other adduct bands, and
it is the most red shifted band from the atomic resonance transition for the 1:1 Sr⋯OH₂ adduct suggesting that it may be associated with the most stable excited state of the adduct. In view of these analogous associations and the arguments presented in the Ca-H₂O adduct discussion, the "G" band is tentatively assigned to the ¹B₂ + ¹A₁ transition of the adduct. Although the ¹B₂ state diabatically arises from a symmetry splitting of the p orbital degeneracy, adiabatically it correlates into the M*(¹D) + H₂O(¹A₁) combination due to an avoided surface crossing previously described. The assignments that correspond to the "C", "D", "E", and "F" bands are not unambiguous since selective photolysis studies were unsuccessful in deconvoluting their interrelationships. However, in analogy to the Ca⋯OH₂ adduct study, these bands probably can be associated with transitions to a ¹A₁ state and perhaps several ¹B₁ states. Multiple ¹B₁ states probably correspond to different out-of-plane geometric isomers of the adduct. Multiple matrix sites may also be further complicating this analysis.

e. BARIUM AND WATER

Band intensity behavior observed during the selective photolysis studies of the Ba⋯OH₂ bands suggests that the adduct has two excited electronic states one of which is split forming a band cluster. The analysis of the electronic
structure of the Ba····OH₂ adduct is simplified by the absence of the low energy ¹D state in the vicinity of the ¹P state which complicated the interpretation of the electronic structure of the Ca- and Sr-H₂O adducts. The ¹D state is too low in energy (less than 11,000 cm⁻¹) to be apparent in the U.V.-VIS spectra. According to preliminary considerations, the absence of the ¹D state means the Ba····OH₂ adduct should have only two stable excited electronic states, ¹B₂ and ¹B₁, which should correlate with the two systems of matrix transitions. Since the ¹B₂ state is believed to be the most stable, the "H" band can be tentatively assigned to a ¹B₂ + ¹A₁ transition for the adduct, and by elimination, the "C", "D", "E", "F", and "G" bands can be tentatively assigned to a ¹B₁ + ¹A₁ transition for the adduct. These states correlate adiabatically into the M⁺(¹P) + H₂O(¹A₁) combination since there is no avoided surface crossing with other ¹B₂ or ¹B₁ potential surfaces. Although the splitting noted for the ¹B₁ + ¹A₁ transition may be partially understood in terms of matrix site effects, some of the bands are probably attributable to different geometric isomers of the Ba-H₂O adduct as was noted for the Ca-H₂O adduct. Different geometric conformations of the adduct that would split the ¹B₁ state without perturbing the ¹B₂ state correspond to the metal tilting out of the plane defined by the water molecule breaking the C₂v
symmetry for $C_8$ symmetry. Any out-of-plane tilt would destabilize the $^1B_1$ state since the tilt would enhance the electron repulsion between the $b_1$ orbital of the metal and the $b_1$ orbital of water; therefore, the "G" band may correspond to a $^1B_1 + ^1A_1$ transition for a $C_{2v}$ adduct whereas the "G" band may correspond to a very bent geometric isomer for the adduct. Since Ba has very low energy empty d and p orbitals which have $b_1-a'$ symmetry components that may mix with the filled $b_1-a'$ orbital of water, it is reasonable to expect stable geometric isomers for the adduct of $C_8$ symmetry.

Figure III-7 shows that deuterium substitution not only red and blue shifted the adduct bands but also significantly increased some of their intensities. As was previously discussed, the red and blue shifts can probably be interpreted in the context of differing zero point energy shifts for the $A_1$, $B_1$, and $B_2$ vibrational modes in the ground and the excited states; however, the lack of quantitative information regarding these vibrational frequencies in the different states precludes any further analysis. The dramatic intensity changes for the "F" and "D" bands is interesting and was not observed for the other metal-water adduct bands. It may be suggested that these bands correspond to two different out-of-plane geometric isomers which have such shallow potential energy wells that lowering
the zero point energy level for the \( B_\perp \) vibrational mode via
deuterium substitution is effective in significantly
stabilizing these particular conformations. This interpre-
tation for the observed isotopic behavior is in keeping with
the conjectured isomeric origin of the band cluster, and
the calculated shallowness of the potential energy well for
the out-of-plane configuration of the \( \text{Be} \cdots \text{OH}_2 \) adduct.

Table III-5 lists dissociation energy estimates for
several excited states of the \( \text{Ba} \cdots \text{OH}_2 \) adduct in solid
krypton. The \( ^1B_2 \) state and the most stable \( ^1B_\perp \) state have
dissociation energies of 4,833 cm\(^{-1}\) + \( D_0^" \) and 2,970 cm\(^{-1}\) + \( D_0^" \),
respectively. These energies can not be meaningfully com-
pared to the \( ^1B_2 \) and the \( ^1B_\perp \) states for the \( \text{Ca} \)- and \( \text{Sr} \)-\( \text{H}_2\text{O} \)
adducts since the latter adducts dissociate into the
\( \text{M}^\#(^1\text{D}) + \text{H}_2\text{O}(^1\text{A}_\perp) \) combination; however, the general quali-
tative agreement of the dissociation energies is good among
these experimental systems as well as when compared to the
\textit{ab initio} dissociation energies calculated for other
metal–water complexes (see Table III-1). The 1,863 cm\(^{-1}\)
energy spacing between the \( ^1B_2 \) and \( ^1B_\perp \) states for \( \text{Ba} \cdots \text{OH}_2 \)
is also in good agreement with other \( B_2 - B_\perp \) separations
evaluated experimentally (1,675 cm\(^{-1}\) for \( \text{Ca} \cdots \text{OH}_2 \)) and
through quantum–chemical techniques (1,500 cm\(^{-1}\) and 1,855 cm\(^{-1}\)
for \( \text{Li} \cdots \text{OH}_2 \)^\# and \( \text{Al} \cdots \text{OH}_2 \), respectively).
2. ORBITAL AND STATE CORRELATIONS

The reaction dynamics of the Group IIA metal-water chemistry may be interrogated in the light of orbital and state correlations which may elucidate the reaction pathways that are photolytically induced. Initially, it is appropriate to examine the evolution of the molecular orbital structure of the reactants into the MO structure of the products that allows one to evaluate the electron configurations, and hence the electronic states, of the products that are generated by chemical reaction. A suitable molecular orbital correlation diagram for the investigation of magnesium-water interactions is shown in Figure III-11. This MO correlation diagram analyzes the metal atom approaching the water molecule along the perpendicular bisector of the O-H bond so the system remains in the $C_1$ point group even with in-plane deviations from the perpendicular bisector. It is reasonable to believe that the $C_{2v}$ adduct precursor must rearrange to this $C_2$ approach before the insertion reaction may occur.

The molecular orbital structure of the HMgOH species is expected to be quite similar to a bent HAB molecule /18/ identifying the OH fragment with the B atom. The ground state electron configuration for the ten electron HMgOH species is expected to be

$$\ldots (1a'')^2(6a')^2$$
FIGURE III-11

MOLECULAR ORBITAL CORRELATION DIAGRAM FOR THE MAGNESIUM–WATER INTERACTIONS
which corresponds to a \( ^1A' \) electronic ground state with a doubly occupied highest occupied molecular orbital. The first excited electron configuration is expected to be

\[ \ldots \ (1a'')^2(6a')(7a') \]

which corresponds to a \( ^1A' \) excited electronic state that is predictably quite high in energy above the ground \( ^1A' \) state since (1) no bands attributable to HMGH were observed in the U.V.-VIS spectra, and (2) light of \( \lambda \geq 2000 \) Å was unsuccessful in dissociating the HMGH to form MgOH + H in the IR studies as it was for the Sr and Ba insertion products. In the \( C_s \) approach, the filled 4s-a' orbital of Mg correlates into the 6a' orbital for HMGH. The unfilled 4a_1-a' antibonding valence orbital of water correlates into the 7a' orbital for HMGH. According to this orbital occupancy, a \( ^1A' \) potential energy surface is generated which correlates the Mg(\( ^1S \)) + H\(_2\)O(\( ^1A_1 \)) reactants into the \( ^1A' \) ground state of HMGH (see Figure III-12). Table III-6, which tabulates the heats of reaction for \( M + H_2O + HMOH \), indicates that this correlation is an exothermic process. The correlation diagrams indicate that no potential energy barrier is encountered along this surface; however, a small barrier predictably exists since some promotional energy is required to break up the s orbital electron pair and s-p hybridize. Curtiss and Frurip /9/ have carried out limited calculations
FIGURE III-12

ELECTRONIC STATE CORRELATION DIAGRAM FOR THE MAGNESIUM–WATER INTERACTION

--- DENOTES STATES WHICH HAVE NOT BEEN OBSERVED

0 DENOTES AN AVOIDED SURFACE INTERSECTION
which also indicate that there exists a barrier to insertion of the Mg and Be metal atoms into the water molecule; therefore, isolation of the $\text{Mg} \cdots \text{OH}_2$ adduct is expected. Figure III-12 shows that the metal-water interaction splits the $\text{^1P}$ excited state degeneracy into a $\text{^1A''}$ excited state and two $\text{^1A'}$ states one of which adiabatically correlates into the $\text{^1A'}$ excited state of $\text{HMgOH}$; however, the molecular orbital correlations indicate the diabatic correlation of the $\text{^1P-^1A'}$ state is to a higher product $\text{^1A'}$ state but encounters an avoided surface intersection with a $\text{^1A'}$ charge transfer surface generating a potential energy barrier to insertion along this surface. Consequently, this excited $\text{^1A'}$ potential surface is not expected to be responsible for the insertion reaction. The insertion reaction probably then evolves along the ground $\text{^1A'}$ potential surface since the excited states of $\text{HMgOH}$ are too high in energy to allow a exothermic correlation from the metal's excited $\text{^1P}$ state to the lowest energy excited states of $\text{HMgOH}$ along $\text{^1A'}$ or $\text{^1A''}$ potential surfaces. Since bonding for the magnesium-water complex is much greater in the excited state as opposed to the ground state (800 cm$^{-1}$ versus 8,500 cm$^{-1}$), large off-diagonal Franck-Condon factors probably exist for the $\text{^1B}_2 \leftrightarrow \text{^1B}_1 \leftrightarrow \text{^1A}_1$ adduct transition which in emission creates a vibrationally excited adduct. Since excited states are stable with respect to reaction, this excess vibrational energy is probably
effective in overcoming any small potential energy barrier and driving the reaction down the ground \(^1\text{A}'\) potential surface.

The molecular orbital and electronic state correlations for the Ca-, Sr-, and Ba-H\(_2\)O systems are significantly different than those for the Mg-H\(_2\)O system. The ns-a' orbital has a lower ionization energy that positions it above water's \(^4\text{a}_1\)-a' orbital. This unfilled orbital correlates into the 6a' HOMO whereas the filled ns-a' orbital correlates into the 7a' LUMO of HMOH. According to these orbital occupancies, two A' potential surfaces are generated: (1) an A' surface which correlates the ground state reactants, M\((^2\text{S}) + \text{H}_2\text{O}(^1\text{A}_1)\), into the \(. . . (1a''')^2(6a')^2(7a')\) excited electron configuration of HMOH and (2) an A' surface that correlates excited reactants, M\(^+2\) + H\(_2\)O\(^-2\), into the \(. . . (1a''')^2(6a')^2\) ground state configuration for HMOH. A pure state correlation indicates the ground states of the reactants and products correlate; however, illuminating this with the MO correlations allows one to predict a significant potential energy barrier to reaction along the ground potential surface generated by an avoided surface intersection of the two A' surfaces. The photochemical pathways that may exist from excited states of the adduct to the insertion product are not unambiguous due to the more important role the d orbitals play in the electronic
structures of these species for Ca, Sr, and Ba which severely complicates state and orbital correlations. However, the fact that photolysis of the metal-water adduct generated the MOH radicals for \( M = \text{Ca, Sr, and Ba} \) but not for Mg may suggest that a different pathway is followed by the heavier Group IIA metals, perhaps along an excited potential surface. The heats of reaction for MOH formation from \( M + \text{H}_2\text{O} \), shown in Table III-6, are very similar for Mg, Ca, and Sr which suggests that lack of MgOH formation probably can not be rationalized in terms of simple thermodynamics. In general the Mg-H\(_2\)O insertion reaction is expected to proceed along the ground \( ^1\text{A'} \) potential surface, whereas there is strong reason to believe a potential energy barrier exists along this same ground \( ^1\text{A'} \) surface for the Ca-, Sr-, and Ba-H\(_2\)O systems which may preclude a ground state reaction.
REFERENCES


17. L.A. Curtiss and D.J. Frurip, Private Communication.


CHAPTER FOUR

ELECTRONIC MATRIX ISOLATION SPECTROSCOPIC STUDIES OF
THE GROUP IIIA METAL–WATER PHOTOCHEMISTRY
CHAPTER FOUR

OUTLINE

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IV. ELECTRONIC MATRIX ISOLATION SPECTROSCOPIC STUDIES OF THE GROUP IIIA METAL-WATER PHOTOCHEMISTRY

A. INTRODUCTION

Much recent interest has attended the characterization of the oxidative Group IIIA metal atom hydration reaction intermediates and products. Margrave and co-workers /1/ have performed infrared matrix isolation studies of the interactions of Group IIIA metal atoms with water demonstrating that Al atoms spontaneously undergo oxidative insertion to form the divalent HMOH species, whereas Ga, In, and Tl atoms form the M⋯OH₂ adduct or complex as evidenced by a decrease in the v₂ bending mode frequency of water. Upon photolysis, each of these adducts except for Tl⋯OH₂ forms the divalent hydroxy metal hydride, HMOH, and extended photolysis of the HMOH molecules generates the monovalent metal monohydroxides, MOH.

Theoretical calculations /2,3,21/ have been performed on the M⋯OH₂ and HMOH molecules to evaluate their stabilities, geometries, and reaction pathway potential energy barriers. Preliminary results of Kurtz and Jordan /2/ indicate that the HALOH molecule is nonlinear, experiences no potential energy barrier upon formation from Al + H₂O, and is stable by at least 38 kcals/mole relative
to Al + H₂O. These theoretical predictions are corroborated by experimental results. Margrave and co-workers /1/ observed spontaneous insertion of the Al atom into the OH bond of H₂O to form the HALOH species having C₅ symmetry. Oblath and Gole /4/ proposed that the excited HALOH molecule is one of several plausible candidates to explain the white-blue chemiluminescent emission continuum emanating from the oxidative interaction of aluminum and water vapors under single and multiple collision conditions.

Finally, there is some controversy surrounding the characterization of the visible chemiluminescent continuum emitter observed upon gas phase oxidation of aluminum or aluminum-containing compounds. In particular, upper atmospheric (90-220 km) seeding studies of winds, diffusion, temperature, and other atmospheric properties involve the release of trimethyl aluminum (TMA) or the explosion of aluminum grenades in the upper atmosphere which at nighttime generates a chemiluminescent glow characterized by an unresolvable emission continuum. This chemiluminescent continuum has been reproduced in a number of laboratories, and a variety of suggestions with regard to the nature of the continuum emitter have been forwarded.

Oblath and Gole /4/ have reviewed these aluminum oxidation studies whose combined work encompasses a wide variety of potential upper atmospheric oxidizers.
However, only Oblath and Gole /4/ have investigated the oxidative gas phase hydration of aluminum vapors, finding that the interaction, under single and multiple collision conditions, generates a weak chemiluminescent flame having a spectrum very reminiscent of the upper atmospheric glows. Further investigation of other oxidizers (O₂, SO₂, CO₂, and H₂O₂) interacting with aluminum vapors yielded no observable chemiluminescence. In contrast, previous studies /5/ of the reaction of aluminum vapors with N₂O, O₂, and CO₂ gases reported the observation of chemiluminescence similar to the upper atmospheric glows. Oblath and Gole note that intrinsic to the detection of fluorescence is an enhanced sensitivity to contamination and suggest that previous investigations /5/ may have been plagued by water contamination. They also point out that most of the water vapor present in the upper atmosphere is deposited by the payload rockets dispersing the TMA and aluminum grenades. Based on the limited possibilities for the emitter from the single collision results and after a consideration of reaction and excited state energetics, Oblath and Gole /4/, in conjunction with matrix isolation studies, suggest that the continuum emitter is a complex involving aluminum and several water molecules or a 1:1 aluminum-water adduct that rearranges to form aluminum hydroxy-hydride in an excited state, HA1OH*.  

*
In view of the matrix isolation infrared studies, the theoretical calculations, and the studies of aluminum beam-water reactions, it is of considerable interest to probe the electronic structures of the Group IIIA metal atom hydration reaction intermediates and products isolated in rare gas matrices. Such a study will form a useful adjunct to the infrared research since it will probe the perturbation of the metal atom's electronic structure upon interaction with a water molecule. A mapping of the electronic structure of these species will provide a data set to which further theoretical calculations may compare. A more focused elucidation of the nature of the gas phase aluminum hydration reaction's chemiluminescent continuum emitter may be provided since the HA\textsubscript{OH} molecular species may be isolated and spectroscopically analyzed in a rare gas matrix, and its stability may be probed by selective photolysis. In addition, this study will report the spectra of MOH molecules, which are photolytic products of the HMOH species. There is interest in the electronic structures of the MOH molecules since they are members of the HBA class of compounds where B is more electronegative than A \cite{6}. Quantum-chemical calculations predict the first electronically excited states of AlOH are at least 30,000 cm\textsuperscript{-1} above the $^1\Sigma^+$ ground state \cite{6}.\textsuperscript{6}
B. EXPERIMENTAL

Aluminum metal was obtained from Bakers, Inc. and was of 99.9%+ purity. Gallium metal was acquired from Alfa Inorganic at 99.9%+ purity. Indium metal was procured from the laboratory at an unknown purity. The aluminum metal was vaporized from a molybdenum cylindrical cell with carbon spacing rings to support the cell in a resistively heated, one-mil Ta foil furnace assembly. The gallium and indium metals were vaporized from alumina cylindrical crucibles. The furnace-cell assembly was outgassed for two hours prior to deposition at a temperature that corresponded to a vapor pressure of $10^{-4}$ torr for the particular metal to be studied. System pressure after cooldown and oven outgassing was less than $1 \times 10^{-7}$ torr. Host-to-guest ratios in the matrices were measured with the quartz crystal microbalance and will be reported for each experiment. Each cryogenic solid matrix sample required 15 minutes to prepare.

C. RESULTS

1. ALUMINUM AND WATER

Cocondensation of aluminum atoms with water molecules at 15K in an excess of krypton generates a transparent, colorless solid matrix.
Figure IV-1 shows the electronic absorption spectra corresponding to four experiments: Al/Kr; Al/H₂O/Kr; Al/H₂O/Kr + hv; and Al/D₂O/Kr. Table IV-1 lists the assignments corresponding to band maxima for each of these spectra. Figure IV-1(A) shows the strongly allowed electronic resonance transitions of the Al atom. Comparison with gas phase transition energies /8,9/ allows assignment of the peaks denoted by "A" to the 4s(²S) + 3p(²P) resonance transition and "B" to the 3d(²D) + 3p(²P) atomic transition. The major "A" and "B" peaks are blue shifted by 1900 cm⁻¹ and 500 cm⁻¹, respectively, relative to their respective gas phase transitions. These expected matrix blue shifts are attributable to a strongly repulsive matrix interaction in the atom's excited state /10/. Subordinate "A" and "B" bands may be attributed to the Al atom residing in multiple and/or low symmetry trapping sites since a series of dilution and contaminant dopant (O₂, CO, H₂O) studies show no relative change in these peak intensities. ESR results /11,13/ indicate that the Al atom is isolated in three different sites in the Kr matrix solid. These assignments basically concur with those made by Ammeter and Schlossnagle /11/ for atomic aluminum. However, at higher dilutions (Kr:Al > 1000) the "C" bands disappear yet the "D" bands persist at the same intensity relative to the other atomic bands. Also,
FIGURE IV-1

U.V.-VIS ABSORPTION SPECTRA FOR ALUMINUM AND WATER ISOLATED IN A KRYPTON MATRIX

(A) Al:Kr = 1:500

(B) Al:H₂O:Kr = 1:10:675

(C) Same as (B) but photolyzed for five minutes with light of $\lambda > 3000$ Å

(D) Al:D₂O:Kr = 1:3.5:350
### Table IV-1

Assignments for the optical absorption spectra of the Al/Kr, Al/H₂O/Kr, Al/H₂O/Kr + hν, and Al/D₂O/Kr systems

<table>
<thead>
<tr>
<th>PEAK</th>
<th>λ(Å)</th>
<th>SPECIES</th>
<th>ASSIGNMENT$^f$</th>
<th>GAS PHASE$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(cm⁻¹)</td>
<td></td>
<td></td>
<td>(cm⁻¹)</td>
</tr>
<tr>
<td>A</td>
<td>3902</td>
<td>A1</td>
<td>4s(2s)+3p(2p)</td>
<td>25 348</td>
</tr>
<tr>
<td>A</td>
<td>2695</td>
<td>A1</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>A</td>
<td>2651</td>
<td>A1</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>B</td>
<td>3292</td>
<td>A1</td>
<td>3d(2D)+3p(2p)</td>
<td>32 435</td>
</tr>
<tr>
<td>B</td>
<td>3122</td>
<td>A1</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>B</td>
<td>3040</td>
<td>A1</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>B</td>
<td>3002</td>
<td>A1</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>C</td>
<td>4083</td>
<td>Al2</td>
<td>B(1Σ⁺ₓ)(n,0)²ₓ X(1Σ⁺ₘ)</td>
<td>?</td>
</tr>
<tr>
<td>C</td>
<td>4039</td>
<td>Al2</td>
<td>B(1Σ⁺ₓ)(n+1,0)²ₓ X(1Σ⁺ₘ)</td>
<td>?</td>
</tr>
<tr>
<td>C</td>
<td>4001</td>
<td>Al2</td>
<td>B(1Σ⁺ₓ)(n+2,0)²ₓ X(1Σ⁺ₘ)</td>
<td>?</td>
</tr>
<tr>
<td>C</td>
<td>3964</td>
<td>Al2</td>
<td>B(1Σ⁺ₓ)(n+3,0)²ₓ X(1Σ⁺ₘ)</td>
<td>?</td>
</tr>
<tr>
<td>D</td>
<td>2624</td>
<td>Al</td>
<td>5s(2S)+3p(2p)</td>
<td>37 689</td>
</tr>
<tr>
<td>D</td>
<td>2401</td>
<td>Al</td>
<td>4d(2D)+3p(2p)</td>
<td>38 929</td>
</tr>
<tr>
<td>E</td>
<td>2744</td>
<td>Al₂O</td>
<td>A(000)+X(000)⁴</td>
<td>?</td>
</tr>
<tr>
<td>E</td>
<td>2696</td>
<td>Al₂O</td>
<td>A(110)+X(000)</td>
<td>?</td>
</tr>
<tr>
<td>E</td>
<td>2677</td>
<td>Al₂O</td>
<td>A(200)+X(000)</td>
<td>?</td>
</tr>
<tr>
<td>F</td>
<td>2849</td>
<td></td>
<td>IMPURITY</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>4524</td>
<td>HA1OH</td>
<td>A(2A''')+X(2A')</td>
<td>~20 000</td>
</tr>
<tr>
<td>H</td>
<td>4576</td>
<td>AlO</td>
<td>B(2Σ⁺)(Q0)X(2Σ⁺)</td>
<td>20 635⁴</td>
</tr>
<tr>
<td>H</td>
<td>4400</td>
<td>AlO</td>
<td>B(1Q)X</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>2486</td>
<td>Al₁OH</td>
<td>A(1Πₚ)+X(1Σ⁺)</td>
<td>?</td>
</tr>
<tr>
<td>J</td>
<td>6993</td>
<td>Al₂</td>
<td>A(1Πₜ)+X(1Σ⁺)</td>
<td>?</td>
</tr>
</tbody>
</table>

$^{a}(v',v'')$. $^{b}$From refs. 8, 9, and 12. $^{c}$±15 cm⁻¹.

$^{d}(v₁,v₂,v₃)$. $^{e}_{v_{oo}}$. $^{f}$Energies of transition are taken from band maxima unless noted otherwise.
upon annealing, the 3902 Å, "A" band disappears revealing a previously buried, weak third "C" band at 3968 Å forming a Franck-Condon envelope with an average $\Delta G_{\nu+1}$ of 245 cm$^{-1}$. Careful concentration studies are instrumental in determining the assignment for the "C" bands and will be presented shortly. In view of their triplet structure, which is similar to the other Al resonance transitions, and their concentration dependence, the "D" bands are tentatively assigned to the $5s(^2S) + 3p(^2P)$ and $4d(^2D) + 3p(^2P)$ atomic resonance transitions. The large line width is probably partially due to the overlapping of the two transitions. The "E" bands correspond to vibronic transitions for the $\text{Al}_2\text{O}$ molecule /7/ which is generated by the molten aluminum metal reducing the aluminum sesquioxide impurity residing in the metal sample. Extended operation of the furnace discriminated against these bands. From dilution and contaminant dopant experiments, the "F" band could not be associated with any of the other bands; however, it did decrease in intensity when the oven was operated at slightly lower temperatures. This band has also been observed in other metal atom matrix isolation experiments in this laboratory where alumina spacers were utilized at high temperatures. This band is presently left unexplained.

In Figure IV-1(B), the band denoted by "G" may be
assigned to the reaction product of aluminum and water which, in collaboration with previous infrared studies /1/, may be identified with the HAlOH molecule. This very broad absorption has a short wavelength onset at ~4000 Å, maximizes at ~4500 Å, and tails out to ~6300 Å. This absorption correlates well with the densely structured chemiluminescent continuous emission spectra observed in beam-gas experiments involving the hydration of aluminum which typically ranged from 3500 Å to 8000 Å, peaking out at about 4500 Å. Due to the enhanced sensitivity to weak spectroscopic features intrinsic to fluorescence detection, it is easy to understand a discrepancy in the red cutoff when compared to the absorption technique. The Kr:H₂O ratio was varied from 300:1 to 65:1 while maintaining the Kr:Al ratio at 650:1. Over this concentration range, only the "G" band was observed whose intensity was maximized at a ratio of 110:1. At higher concentrations the band diminished in intensity which is perhaps indicative of a higher order water-metal interaction. Neither the water concentration nor annealing studies noticeably changed the structure of the "G" band. Photolysis of the "G" band with light having a 4500 Å short wavelength cutoff (Corning 3-72 + water-Pyrex filters) for ten minutes caused no change in the band structure. Figure IV-1(C) shows that a five minute photolysis with light having a 3000 Å short wavelength
cutoff (water-Pyrex filter) destroys the "G" band totally generating the "H" and "I" bands. The "H" bands are assigned to the A10 molecular species since the peak positions correlate very well with previous matrix isolation studies of the B^2\Sigma^+ + X^2\Sigma^+ system for A10 /13/. The "I" band is assigned to a transition of the A10H molecule since A10H is the major photolysis product noted in the infrared matrix studies /1/, this band is similar in energy to the analogous gas phase A1F diatomic A^1\Pi + X^1\Sigma^+ system (T_e = 43,949 cm\(^{-1}\)) /12/, and quantum-chemical calculations indicate the lowest-lying excited states of A10H lie at energies in excess of 30,000 cm\(^{-1}\) above the ground 1\Sigma^+ state /4,6/. The A excited state of A10H is predictably a 1\Pi state in analogy to the 1\Pi first excited singlet state of the A1F diatomic. The "G" band in Figure IV-1(D) is assigned to the DA10D molecule which is identical in structure to the HAlOH molecule except for superimposed A10 B^2\Sigma + X^2\Sigma "H" bands. Evidently DA10D formation is accompanied by A10 formation whereas HAlOH is not. Further study is needed to understand this phenomena.

Figure IV-2 shows an electronic absorption trace corresponding to an experiment with a higher concentration of aluminum atoms in the krypton solid such that the Kr:Al ratio was 180:1. From this higher concentration study,
FIGURE IV-2

U.V.-VIS ABSORPTION SPECTRUM FOR ALUMINUM DIMERS
ISOLATED IN A KRYPTON MATRIX
a fourth "C" band in the vibronic progression became perspicuous along with the broad "J" band centered around 14,300 cm\(^{-1}\). This "J" band along with the "C" band progression is assigned to an electronic transition of the molecular aluminum dimer for two reasons: (1) in the course of increasing the aluminum metal concentration in the krypton solid, these bands were the first to grow in after the atomic aluminum resonance absorption features, and (2) careful concentration studies show that both the "J" and the "C" bands grew in according to the second power of the metal deposition rate established by the quartz crystal microbalance. A gas phase study of the emissions from the aluminum dimer out of a King furnace reports the observation of a \(^3\Sigma^-_u \rightarrow \ ^3\Sigma^-_g\) system at 17,234 cm\(^{-1}\) for the (0,0) transition /24/. The detailed nature of the states involved in this emission system were derived partially from molecular orbital theory. The \(^3\Sigma^-_u\) state has an \(\omega_e\) value equaling 279 cm\(^{-1}\), while the \(\omega_e\) value for the \(^3\Sigma^-_g\) state is 350 cm\(^{-1}\). From this gas phase study, the authors tentatively identify the electronic ground state of Al\(_2\) with the lower \(^3\Sigma^-_g\) state observed in emission. However, neither the matrix A + X electronic transition nor the matrix B + X transition for Al\(_2\) may be identified with the gas phase \(^3\Sigma^-_u \rightarrow \ ^3\Sigma^-_g\) system because (1) the red and blue shifts of the A and B states that would have to correspond in identification with this
system are too large in magnitude to be reasonable, and (2) the matrix B state has a $\Delta G'_{\nu+1}$ average value of 245 cm$^{-1}$ that does not correlate well with the 279 cm$^{-1}$ $\omega_e$ value for the $3\Sigma_u^-$ state. Therefore, because (1) it is reasonable to assume that electronic absorptions observed in the matrix solid originate from the electronic ground state of a molecular or atomic species, and (2) the gas phase emission system can not be identified with any matrix absorption system, the lower state observed in the gas phase emission of Al$_2$ can not be identified with the ground state, and thus the electronic ground state assignment and its corresponding ground state electron configuration are probably incorrect. Possible assignments for the ground electron configuration and electronic state of the aluminum dimer will be detailed in the discussion section of this chapter.

2. GALLIUM AND WATER

Cocondensation of Ga atoms with H$_2$O molecules at 15 K in an excess of Kr generates a transparent, colorless matrix.

Figure IV-3 shows the electronic absorption spectra corresponding to three experiments: Ga/Kr; Ga/H$_2$O/Kr; and Ga/H$_2$O/Kr + hv. Table IV-2 lists the assignments corresponding to band maxima for each of these spectra.
FIGURE IV-3

U.V.-VIS ABSORPTION SPECTRA FOR GALLIUM AND WATER ISOLATED IN A KRYPTON MATRIX

(A) $\text{Ga:Kr} = 1:1150$ (Ga$_2$ assignment made from other spectra)

(B) $\text{Ga:H}_2\text{O:Kr} = 1:5:1280$

(C) Same as (B) but photolyzed for five minutes with light of $\lambda > 3000 \text{ Å}$
    (GaOH assignment made from other spectra)
<table>
<thead>
<tr>
<th>PEAK ( \lambda ) (Å)</th>
<th>SPECIES</th>
<th>ASSIGNMENT</th>
<th>GAS PHASE (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 3990</td>
<td>Ga</td>
<td>5s(^2\text{S})+4p(^2\text{P})</td>
<td>24 788</td>
</tr>
<tr>
<td>A 3761</td>
<td>Ga</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>A 3679</td>
<td>Ga</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>B 3341</td>
<td>Ga(_2)</td>
<td>(4d(^2\text{D})+4p(^2\text{P})); B((1\Sigma^+)+X((1\Sigma^+))</td>
<td>34 782;?</td>
</tr>
<tr>
<td>B 3141</td>
<td>Ga</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>B 3111</td>
<td>Ga</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>B 2720</td>
<td>Ga</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>C 6413</td>
<td>Ga(_2)</td>
<td>A((1\Pi_u)+X((1\Sigma^+))</td>
<td>?</td>
</tr>
<tr>
<td>D 4922</td>
<td>Ga(_2)OH(_2)</td>
<td>A((2A_1)+X((2\Sigma^+))</td>
<td>?</td>
</tr>
<tr>
<td>D 4547</td>
<td>Ga(_2)OH(_2)</td>
<td>&quot;</td>
<td>?</td>
</tr>
<tr>
<td>E 2555</td>
<td>GaOH</td>
<td>A((1\Pi)+X((1\Sigma^+))</td>
<td>?</td>
</tr>
</tbody>
</table>

\(^a\)± 15 cm\(^{-1}\).

\(^b\)From refs. 8, 9, and 12.

\(^c\)Energies of transition are taken from band maxima unless noted otherwise.
Figure IV-3(A) shows the strongly allowed electronic resonance transitions for the Ga atom. In a manner analogous to aluminum, bands "A" and "B" are assigned to the $5s(^2S) \rightarrow 4p(^2P)$ and the $4d(^2D) \rightarrow 4p(^2P)$ gallium atomic resonance transitions, respectively. For the major "A" and "B" bands, blue shifts of 2391 cm$^{-1}$ and 1983 cm$^{-1}$ are observed from their respective gas phase transitions. As with Al, the "A" and "B" bands are triplet in nature which is undoubtedly accountable in terms of multiple sites and/or crystal field removal of orbital degeneracy. ESR results indicate that the Ga atom resides in two different sites in a Kr solid. As with aluminum, the long wavelength "A" band is discriminated against by annealing or localized heating via photolysis. These assignments agree with those made by Ammeter and Schlossnagle /11/ for Ga atoms isolated in a Kr matrix. However, it should be noted that their spectra for Al and Ga are plagued by light scattering in the deep UV which in the case of Al made it impossible to see the $5s(^2S) \rightarrow 3p(^2P)$ and the $4d(^2D) \rightarrow 3p(^2P)$ transitions. Referencing the host matrix with the spectrometer made these as well as other absorptions in the deep ultraviolet distinct in these studies. Their bands for Al in a Kr matrix at 4 K are much broader than in this study. Although they report red shifts upon warming the rare
gas solid to 20 K, no mention is made of band sharpening. Our energy assignments for the $^2S + ^2P$ transitions of Ga and Al almost perfectly concur when compensation is made for the blue shift in taking the rare gas solid from 15 K to 4 K. However, the agreement is not as good for the energy assignments of the $^2D + ^2P$ transitions of Al and Ga, especially for the subordinate "B" peaks indicating that these peaks may be quite temperature sensitive. The 3341 Å "B" band has a peculiar concentration dependence in that at higher concentrations it grows in much more rapidly than the other monomeric "B" bands; however, at very high dilutions where no metal clusters are expected to have formed, this "B" band still persists with relatively good intensity. The concentration dependence of this band is a little less than the second power of the metal deposition rate. Therefore, it is quite possible that a Ga dimer electronic transition overlaps the 3341 Å Ga atomic transition. Band "C" may be assigned to the Ga$_2$ molecule since concentration studies show it is the first peak to grow in after the atomic bands, and its growth is a precise quadratic function of the metal deposition rate. In the gas phase, emission bands in the region from 18200 cm$^{-1}$ to 21700 cm$^{-1}$ were observed for Ga$_2$ /12/ which if the transitions are identical indicates the dimer spectra is red shifted in the matrix by about 4500 cm$^{-1}$. Since
this is a surprisingly large shift, the transition observed in absorption in the matrix probably can not be identified with the transition observed in emission in the gas phase. Thus, the lower state observed in emission does not correspond to the ground state of Ga\textsubscript{2}.

In Figure IV-3(B), the bands denoted by "D" may be assigned to the reaction product of gallium and water which, in collaboration with previous infrared studies /1/, may be identified with the Ga\textsuperscript{+}·OH\textsubscript{2} adduct. The nature of the long wavelength "D" shoulder will be discussed in more detail in the next section in view of more extensive photolysis work. The band is symmetric and quite broad having a 1500 cm\textsuperscript{-1} FWHM. Water concentration studies show no change in the spectra over the Kr:H\textsubscript{2}O range of 300:1 to 50:1. A two second photolysis with light of \(\lambda > 4000 \ \text{Å} \) (Corning 3-75 filter) reduces the intensity of the adduct absorption band by 50\%. A ten second photolysis with the same color light totally eliminates the adduct band. No new bands were generated as a consequence of this photolysis; however, a five minute photolysis with the same color light (\(\lambda > 4000 \ \text{Å} \)) generates a blue shoulder on the major "B" band. No change in the intensity of the Ga atomic absorptions is observed except for a slight decrease in the 3390 Å "A" band which is known to be heat sensitive. Figure IV-3(C)
shows the blue shoulder on the 2720 Å "B" band generated by a five minute photolysis with light of \( \lambda > 3600 \, \text{Å} \) (Corning 3-94). The atomic absorptions decrease in intensity. This new "E" band is assigned to GaOH, the final photolysis product observed in the infrared study of metal-water chemistry. The analogous GaF diatomic has its first allowed electronic transition at 47,366 cm\(^{-1}\) in the gas phase /12/. With the consideration that infrared studies show the adduct is initially formed upon cocondensation, and that the "D" bands show very similar photosensitivity as the adduct bands did in the infrared work, the assignment of the "D" band to the adduct is quite plausible. Photolyzing the adduct bands to total depletion generates no new perceivable bands; however, continued photolysis in this same region (\( \lambda > 4000 \, \text{Å} \)) where no bands are perspicuous, generates the product GaOH without decreasing the intensity of the atomic bands. Photolyzing with light of \( \lambda > 3600 \, \text{Å} \) overlaps an atomic band which undoubtedly induces localized annealing allowing the Ga atomic species to escape its site and react with \( \text{H}_2\text{O} \) molecules residing in neighboring sites generating under continuous photolysis the GaOH molecule. In view of these findings, the HGaOH intermediate insertion species probably has an extremely broad absorption band that is difficult to discern by absorption techniques or an
absorption band whose energy is beyond the range of the spectrometer. The former conjecture is in keeping with the observed very broad absorption of the HALOH molecule.

3. INDIUM AND WATER

Cocondensation of In atoms with H_2O molecules at 15 K in an excess of Kr generates a transparent, colorless matrix.

Figure IV-4 shows the electronic absorption spectra corresponding to three experiments: In/Kr; In/H_2O/Kr; and In/H_2O/Kr + hv. Table IV-3 lists the assignments corresponding to band maxima for each of these spectra. Figure IV-4(A) shows the strongly allowed electronic resonance transitions for the In atom. In a manner analogous to aluminum and gallium, bands "A" and "B" are assigned to the 6s(^2)S + 5p(^2)P and the 5d(^2)D + 5p(^2)P indium resonance transitions, respectively. For the major "A" and "B" bands, blue shifts of 1440 cm\(^{-1}\) and 2070 cm\(^{-1}\) are observed from their respective gas phase transitions. The major 2S + 2P transition is not split as it was for Al and Ga and is observed as a doublet. The 2D + 2P transition is observed as a triplet with the major band having a very large linewidth of 6,400 cm\(^{-1}\) FWHM. These results do not agree very well with those made by Duley and Garton /14/ who report that "there is little evidence for any absorption bands which might correspond to
FIGURE IV-4
U.V.-VIS ABSORPTION SPECTRA FOR INDIUM AND WATER
ISOLATED IN A KRYPTON MATRIX

(A) $\text{In:Kr} = 1:500$
(B) $\text{In:} \text{H}_2\text{O:Kr} = 1:10:1560$
(C) Same as (B) but photolyzed for five minutes with light $\lambda > 3000 \text{R}$
### TABLE IV-3
ASSIGNMENTS FOR THE OPTICAL ABSORPTION SPECTRA OF THE
In/Kr, In/H₂O/Kr, AND In/H₂O/Kr + hv SYSTEMS

<table>
<thead>
<tr>
<th>PEAK λ(Å)</th>
<th>ν¹ (cm⁻¹)</th>
<th>SPECIES</th>
<th>ASSIGNMENT</th>
<th>GAS PHASE (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4083</td>
<td>24 494</td>
<td>In</td>
<td>6s(²S)+5p(²P)</td>
</tr>
<tr>
<td>A</td>
<td>3874</td>
<td>25 811</td>
<td>In</td>
<td>&quot;</td>
</tr>
<tr>
<td>B</td>
<td>3309</td>
<td>30 222</td>
<td>In</td>
<td>5d(²D)+5p(²P)</td>
</tr>
<tr>
<td>B</td>
<td>2963</td>
<td>33 755</td>
<td>In</td>
<td>&quot;</td>
</tr>
<tr>
<td>B</td>
<td>2860</td>
<td>34 965</td>
<td>In</td>
<td>&quot;</td>
</tr>
<tr>
<td>C</td>
<td>7692</td>
<td>13 000</td>
<td>In₂</td>
<td>A(¹Π_u)→X(¹Σ⁺₆)</td>
</tr>
<tr>
<td>C</td>
<td>3611</td>
<td>27 691</td>
<td>In₂</td>
<td>B(¹Σ⁺₆)→X(¹Σ⁺₆)</td>
</tr>
<tr>
<td>D</td>
<td>4932</td>
<td>20 274</td>
<td>In⋯OH₂</td>
<td>A(²A₁)→X(²B₂)</td>
</tr>
<tr>
<td>D</td>
<td>4614</td>
<td>21 675</td>
<td>In⋯OH₂</td>
<td>&quot;</td>
</tr>
<tr>
<td>E</td>
<td>2707</td>
<td>36 943</td>
<td>InOH</td>
<td>A(¹Π)→X(¹Σ⁺)</td>
</tr>
</tbody>
</table>

¹±15 cm⁻¹.

²From refs. 8, 9, and 12.

³Energies of transition are taken from band maxima unless noted otherwise.
resonance transitions of In"; however, they note several strong autoionizing transitions. The longest wavelength transition they observe is at 2845 Å which they assign to the $5s5p^2(^4P) + 5s^25p(^2P)$ autoionizing transition that corresponds fairly well to the 2860 Å $5d(^2D) + 5p(^2P)$ resonance transition observed in this study. Duley and Garton state that thicker films are needed to observe the resonance transitions. Since metal atom resonance transitions in the gas phase and in the matrix have very strong oscillator strengths, it is not readily apparent why these authors did not observe them along with the autoionizing transitions. The "C" bands may be attributed to the $\text{In}_2$ molecule in view of their concentration dependence. In the gas phase, emission bands were observed between 16,800 - 20,000 cm$^{-1}$, and absorption bands were observed between 26,000 - 28,000 cm$^{-1}$/12/. The matrix phase B $\rightarrow$ X absorption centered at 27,691 cm$^{-1}$ is in good agreement with the absorption system observed in the gas phase ranging from 26,000 cm$^{-1}$ to 28,000 cm$^{-1}$ which leads one to believe that the transitions are identical. However, identification of the broad matrix A $\rightarrow$ X absorption centered around 13,000 cm$^{-1}$ with the 16,800 cm$^{-1}$ to 20,000 cm$^{-1}$ gas phase emission system is quite dubious
since the red shift of the matrix band is too large to make the correlation reasonable. Therefore, as was noted for the gas phase Al₂ and Ga₂ emission systems, the lower state observed in emission probably does not correspond to the ground state of In₂.

In Figure IV-4(B), the bands denoted by "D" are identified with an electronic transition of the In···OH₂ adduct employing the same reasoning used in the Ga-H₂O system. Photolysis of the red "D" shoulder with light of \( \lambda > 5000 \text{ Å} \) (Corning 3-70 + Pyrex-water filters) for 50 minutes totally eliminates the red "D" band; however, the blue "D" band is left totally intact. Subsequent photolysis with \( 4500 \text{ Å} < \lambda < 4700 \text{ Å} \) light (Corning 3-72 and 7-59 + Pyrex-water filters) for 35 minutes reduces the intensity of the blue "D" band by \(~50\%\) without regenerating the red shoulder; however, a blue "E" shoulder grows in on the 2860 \( \text{ Å} \) "E" band. Further photolysis with light of \( \lambda > 3000 \text{ Å} \) (Pyrex-water filter) totally eliminates the "D" bands generating an increased intensity in the "E" band as seen in Figure IV-4(C). In view of these experiments, one may tentatively conclude the red "D" shoulder is not associated with the blue "D" band. Since the red shoulder is not a photolysis product of the blue "D" band, and water concentration studies show no change in the "D" bands' relative intensities, the
shoulder is probably a site effect corresponding to the In\cdots OH₂ adduct or, perhaps, an adduct of a different geometry. The same is thought to be true for the red shoulder observed in the spectra of the Ga\cdots OH₂ adduct. This and other photolysis work indicates that the In\cdots OH₂ complex has a lower quantum efficiency for conversion to products; although, more careful light intensity measurements should be performed. With reasoning similar to that used in the Ga-H₂O system, the HInOH insertion product is believed to have an extremely broad absorption that is not perspicuous in absorption, and the "E" band is associated with the InOH molecule. The analogous InF diatomic has its first allowed transition at 42,809 cm⁻¹ in the gas phase /12/.

D. DISCUSSION

1. ALUMINUM AND WATER

   a. THE NATURE OF ELECTRONIC TRANSITIONS FOR HALOH

   In view of the very close concurrence of the electronic structure of the HALOH molecule, derived from the matrix isolation visible absorption spectra, with the chemiluminescence features observed in the gas phase oxidation of aluminum vapors in the upper atmosphere /15,16/ and in the laboratory /4/, it is possible to tentatively identify the continuum emitter with the
divalent oxidative insertion product of a 1:1 aluminum hydration reaction, HAlOH.

The nature of the electronic transition for the HAlOH molecule may be derived from an examination of a simple Walsh molecular orbital correlation diagram for a linear and bent HAB molecule /17/ (see Figure IV-5) which identifies the OH fragment with the B atom. The electronic structure of the HAlOH molecule is expected to be closely analogous with other 11 electron HAB species such as the HCO radical which has been extensively studied by spectroscopy. The predicted ground state electron configuration for a bent HAlOH molecule is

\[ \ldots (1a'')^2 (6a')^2 (7a') \]

which corresponds to a \( ^2A' \) electronic ground state. The highest occupied molecular orbital (HOMO) is the \( 2\pi-7a' \) orbital which is singly occupied. Since the \( 7a' \) orbital is lower in energy relative to the \( 2\pi \) degenerate orbitals, the equilibrium geometric configuration for HAlOH is expected to be bent along HAlO which is consistent with experimental /1/ and theoretical /2,3/ results. Jordan and Kurtz /2/ calculate a bond angle of 117°. The electron configuration for the first excited state of HAlOH is expected to be

\[ \ldots (1a'')^2 (6a')^2 (2a'') \]
FIGURE IV-5

WALSH MOLECULAR ORBITAL CORRELATION DIAGRAM FOR LINEAR AND BENT HAB MOLECULES
since this is the lowest-lying excited state configuration for the HCO radical /18/. This configuration corresponds to a $^2A''$ electronic state. Therefore, the $A \rightarrow X$ transition observed in the matrix for HAlOH is predicted to be a symmetry allowed $^2A'' \rightarrow ^2A'$ electronic transition. Since the electronic transition involves vacating the $2\pi-7\alpha'$ orbital, which primarily accounts for the bent configuration of the HAB species /17/, and subsequent occupation of the $2\pi-2\alpha''$ orbital, which is a nonbonding $p$ orbital, the excited state equilibrium geometric configuration is, in all probability, linear which is the case for the first excited state of the HCO radical /19/. In fact, it seems highly probable that the ground and the first excited states for the HAlOH molecule are derived from a Renner-Teller distortion of a doubly degenerate linear $^2\Pi$ state, so the $^2A'$ and $^2A''$ states are $^2\Sigma^+$ and $^2\Sigma^-$ states in the linear conformation. Since the equilibrium bond angle changes dramatically in going from the ground state to the first excited state, the off-diagonal Franck-Condon factors should be of sufficient magnitude to create a long progression in the bending mode that would generate a very broad band for this electronic transition if the vibrational structure can not be resolved. In all probability, this explains the nature of the broad continuum observed experimentally in the matrix absorption
and the chemiluminescent emission studies of the HAlOH molecule.

b. ORBITAL AND STATE CORRELATIONS

The reaction dynamics of the Group IIIA metal-water chemistry may be studied in the light of orbital and state correlations to elucidate the photochemical pathways, the relative reactivities of the different metal systems, and the chemiluminescent processes. Initially, it is appropriate to examine the evolution of the molecular orbital structures of the reactants into the MO structures of the products/intermediates that allow one to determine the electron configurations of the products that are generated by chemical reactions. A suitable molecular orbital correlation diagram for the investigation of Group IIIA metal-water interactions is shown in Figure IV-6. This MO correlation diagram analyzes the metal atom approaching the water molecule in two different dispositions: (1) the metal atom approaching the water molecule along the line defined by the bisection of the water's H-O-H angle so that the system remains in the C_{2v} point group, and (2) the metal atom approaching the water molecule along the perpendicular bisector of the O-H bond so the system remains in the C_{s} point group (even with in-plane
FIGURE IV-6

MOLECULAR ORBITAL CORRELATION DIAGRAM FOR THE
GROUP IIIA METAL-WATER INTERACTIONS
deviations from the perpendicular bisector). This diagram depicts the formation of the metal-water adduct of $C_{2v}$ symmetry, and the HMOH molecule of $C_s$ symmetry. In both approaches, the unfilled $4a_1$ antibonding valence orbital of water correlates into the $7a'$ orbital for HMOH. The degenerate, singly occupied p orbital is split by the interaction into three orbitals one of which is of a" symmetry (out-of-plane p orbital) that correlates into the low-lying 2a" MO of the insertion product. According to this orbital occupancy, a $^2A$" potential energy surface is generated which correlates the $H_2O\quad(^1A_1)$ and the M $(^2P_u)$ reactants in their ground states into the ... $(6a')^2(2a'\prime\prime)$ configuration for the insertion product that corresponds to the $^2A$" excited state observed in absorption and emission (see Figure IV-7). Because the ground state of the insertion product is more stable by about 63 kcal/mole (see Table IV-4) relative to the reactants in their respective ground states, the $^2A$" potential surface that correlates into the $^2A$" excited state of the insertion product is still an overall exothermic process by about 30 kcal/mole and encounters no potential energy barrier to reaction since the state correlation follows directly from the orbital correlation. [Since the red cutoff in the aluminum chemiluminescent flame was around 8000 Å, the difference in the potential
FIGURE IV-7
ELECTRONIC STATE CORRELATION DIAGRAM FOR THE
ALUMINUM-WATER INTERACTION

... DENOTES REPULSIVE STATES
--- DENOTES STATES WHICH HAVE NOT BEEN OBSERVED
0 DENOTES AN AVOIDED SURFACE INTERSECTION
Table IV-4

**ESTIMATED HEATS OF REACTION\(^a\) (kcal/mole)**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al + H_{2}O → HAlOH</td>
<td>-64±10</td>
</tr>
<tr>
<td>Al + H_{2}O → AlO + H_{2}</td>
<td>-5± 2</td>
</tr>
<tr>
<td>Al + H_{2}O → ALOH + H</td>
<td>-12± 5</td>
</tr>
<tr>
<td>Ga + H_{2}O → HGaOH</td>
<td>-34±10</td>
</tr>
<tr>
<td>Ga + H_{2}O → GaO + H_{2}</td>
<td>+26± 2</td>
</tr>
<tr>
<td>Ga + H_{2}O → GaOH + H</td>
<td>+16± 5</td>
</tr>
<tr>
<td>In + H_{2}O → HinOH</td>
<td>-17±10</td>
</tr>
<tr>
<td>In + H_{2}O → InO + H_{2}</td>
<td>+42± 2</td>
</tr>
<tr>
<td>In + H_{2}O → InOH + H</td>
<td>+32± 5</td>
</tr>
</tbody>
</table>

\(^a\)Heats of reaction were estimated using bond energy data from references 12, 28, and 29. Promotional energies were estimated by taking the difference in bond energies for M-OH and M-(OH)$_2$. 
energy well minimums for the $^2A'$ and $^2A''$ states is equal to or less than 35 kcal/mole.] The reactant orbital occupancy that would be required to generate a $^2A'$ surface that would correlate diabatically into the $^2A'$ ground state of the insertion product corresponds to a singly occupied $4a_1$ orbital of water and a vacant 3p orbital of the metal which creates a Coulombic or charge-transfer potential surface derived from the Al$^+$ ($^1S_g$) and H$_2$O$^-$ ($^2A_1$) reactants. The charge-transfer $^2A'$ surface generated by the metal cation and water anion correlates diabatically into the $^2A'$ ground state of HAlOH; however, there is an avoided surface intersection between this $^2A'$ surface and the $^2A'$ surface derived from water's $^1A_1$ state and the metal's $^2P_u$ state where the unpaired electron is in the in-plane p orbital not directed toward the water ($b_2$ orbital in the $C_{2v}$ point group). [The latter $^2A'$ surface diabatically correlates into the first excited $^2A'$ state of HAlOH which, although it has not been documented, is expected to be quite high in energy above the $^2A'$ ground state because of the highly excited electron configuration it requires. For example, the first excited $^2A'$ state of HBF has been calculated to be about 4.6 eV above the ground state /23/.] Therefore, the ground state reactants diabatically correlate into the ground state of the insertion product but only by virtue of an avoided
surface intersection that generates a potential energy barrier to reaction along the ground state $^2A'$ potential energy surface.

These correlations predict two fundamental aspects regarding the reaction dynamics of the Al-H$_2$O interaction that are corroborated by experimental results. Firstly, since the $^2A''$ surface, derived from the reactant $^2A''$ state of Al ($^2P_u$) and H$_2$O ($^1A_1$), correlates without any avoided surface crossings into the $^2A''$ state of HAlOH in an exothermic manner, the Al metal atom should spontaneously insert into the O-H bond which is observed experimentally in the matrix /1/ as well as in the gas phase /4/. Secondly, since the $^2A''$ potential surface is the only unhindered pathway to the insertion product, spontaneous chemical reaction should populate the $^2A''$ excited state causing chemiluminescence from that state which is observed experimentally in the gas phase interaction of aluminum and water vapors in the laboratory and upper atmosphere /4,15,16/.

This analysis depicts the importance of illuminating the results of state correlations with orbital correlations. Although orbital occupancy may predict diabatic state correlations, in an adiabatic process, avoided surface crossings are rigorous which allows one to rationalize the qualitative nature of the potential energy pathway pursued by the reactants. The picture
generated is certainly very crude in nature but quite instrumental in explaining fundamental chemical behavior.

c. PHOTODISSOCIATION OF HALOH

State and orbital correlations are also of great utility in rationalizing photodissociative behavior in molecules. Upon irradiation, the HALOH molecule photodissociates into two pairs of products: (1) HALOH + H and (2) ALO + H₂. Figure IV-8 shows molecular orbital correlations for the HALOH molecule evolving into both pairs of products along the symmetry elements of the Cs point group. The ground state electron configuration of the HALOH molecule correlates into the ground state configurations for the ALOH and H products. Figure IV-9 shows the state correlation diagram for HALOH evolving into ALO + H₂ that includes only the important avoided surface crossings. The 2A' state of HALOH correlates adiabatically into the 2Σ+ state of ALO and the 1Σ₉ state of H₂. The 2A" state of HALOH correlates diabatically into the C²Π state of ALO and the 1Σ₉ state of H₂; however, an avoided surface crossing causes the 2A" state to adiabatically correlate into the A²Π state of ALO and the 1Σ₉ state of H₂ with the formation of a potential barrier to recombination from this product state.
FIGURE IV-8

MOLECULAR ORBITAL CORRELATION DIAGRAM DESCRIBING
THE PREDISSOCIATION OF HMOH TO MO + H₂
AND MOH + H
FIGURE IV-9

ELECTRONIC STATE CORRELATION DIAGRAM DESCRIBING
THE PREDISSOCIATION OF HALOH TO ALO + H₂

0 DENOTES AN AVOIDED SURFACE INTERSECTION
Predissociation of the excited $^2A''$ state of HALOH can take place into the $^2\Sigma^+ + ^1\Sigma_g^+$ or the $A^2\Pi + ^1\Sigma_g^+$ states of the ALO + H$_2$ products since the energy of the second $^2A''$ excited state of the products is much too high. Potentially, HALOH can heterogeneously or homogeneously predissociate into the ALO + H$_2$ products. The $^2A''$ state ($^2\Sigma^-$ in the linear case) of HALOH may heterogeneously predissociate into the $^2A'$ ($^2\Sigma^+$ in the linear conformation) potential energy surface, that correlates with the ALO ($^2\Sigma^+$) + H$_2$ ($^1\Sigma_g^+$) products, by interaction with the out-of-plane torsional mode of A" symmetry. Rotational interaction is not expected to play an important role in this heterogeneous predissociation since rotation for HALOH is probably forbidden in the matrix cage. If sufficiently energetic photons are available, the $^2A''$ state may also homogeneously predissociate ($^2A'' + ^2A''$ for the bent and $^2\Sigma^- + ^2\Sigma^-$ for the linear conformation) into the low-lying $A^2\Pi$ state of ALO and the $^1\Sigma_g^+$ ground state of H$_2$ by following the $^2A''$ potential surface which has a potential energy barrier to recombination generated by the avoided surface crossing. The $A^2\Pi$ state of ALO would then decay to its $^2\Sigma^+$ ground state. From this study, it was not possible to determine the relative importance of the two channels in predissociation.

Figure IV-10 shows the state correlation diagram for HALOH evolving into ALOH + H along $^2A''$ and $^2A'$. 
FIGURE IV-10

ELECTRONIC STATE CORRELATION DIAGRAM DESCRIBING
THE PREDISSOCIATION OF HÀLOH TO ÀLOH + H

0  DENOTES AN AVOIDED SURFACE INTERSECTION
HAIOH

\[ \frac{3\Sigma^+ + 2S_g}{AIOH + H} \]

\[ \frac{3\Pi + 2S_g}{1\Sigma^+ + 2S_g} \]

\[ ^2\Pi \]

\[ ^2\Sigma (\Sigma) \]

\[ ^2\Lambda (\Sigma) \]

\[ ^2\Lambda' (\Sigma) \]

\[ ^2\Lambda'' (\Sigma^-) \]
potential surfaces where only the important surface crossings are depicted. The $^2\text{A}'$ ($^2\Sigma^+$) ground state of HALOH diabatically correlates into ALOH in its highly excited $^3\Sigma^+$ state and H in its $^2\text{S}_g$ ground state following a $^2\text{A}'$ surface. However, this surface is intersected by another $^2\text{A}'$ surface derived from the $^1\Sigma^+ + ^2\text{S}_g$ ground states of the products in an avoided crossing; therefore, the $^2\text{A}'$ ground state of HALOH adiabatically correlates into the $^1\Sigma^+ + ^2\text{S}_g$ ground states for ALOH + H by virtue of an avoided crossing that creates a potential energy barrier to recombination. The $^2\text{A}''$ ($^2\Sigma^-$) excited state of HALOH adiabatically correlates into ALOH in its $^3\Pi$ excited state and H in its $^2\text{S}_g$ ground state. Predissociation of the excited $^2\text{A}''$ state of HALOH must take place into the $^1\Sigma^+ + ^2\text{S}_g$ states of ALOH + H since the energy of the first excited state ($^2\text{A}''$) of the products is much too high. Therefore the predissociation is heterogeneous ($^2\text{A}'' + ^2\text{A}'$ for the bent and $^2\Sigma^- + ^2\Sigma^+$ for the linear conformation) which can arise from interaction of the $^2\text{A}''$ electronic state with HALOH's out-of-plane torsional mode of $A''$ symmetry. There is not a homogeneous pre-dissociative pathway to form ALOH + H from HALOH.

The previous orbital and state correlation analysis can be of assistance in rationalizing certain aspects of the observed photochemistry for HALOH. As previously noted, HALOH did not photodissociate when vigorously
irradiated with light having a short wavelength cutoff at 4500 \( \AA \) (2.75 eV); however, light of \( \lambda > 3000 \\AA \) (4.1 eV) was readily successful in generating both A1O and A1OH products. Figures IV-9 & 10 and Table IV-5 show that at least 2.2 eV of energy must be supplied to HAOH to generate A1OH \( (^{1}\Sigma^+ + H (^{2}\Sigma_g^-)) \), and at least 2.5 eV of energy must be supplied to generate A1O \( (^{2}\Sigma^+ + H_2 (^{1}\Sigma_g^+)) \) (\( \approx 3.2 \) eV is required to access the homogeneous predissociative pathway). Therefore, the 4500 \( \AA \) photolysis was unable to access the heterogeneous predissociative pathways to form A1O and A1OH not because of overall reaction thermodynamics, but probably because this energy of light was insufficient to access the higher vibrational levels of the \( ^2A'' \) excited state that are in the proximity of that portion of the \( ^2A'' \) potential energy surface that intersects the \( ^2A' \) surface where the Franck-Condon factors are of sufficient magnitude to allow heterogeneous predissociation. Certainly, this wavelength of light was energetically insufficient to access the homogeneous predissociative pathway to form A1O + H\(_2\). The more energetic light having a 3000 \( \AA \) (4.1 eV) short wavelength cutoff was sufficient to access those high vibronic states that are appropriately located on the surface so as to strongly couple into the \( ^2A' \) surface causing a heterogeneous predissociation to occur to form both A1O and A1OH. The
TABLE IV-5

ESTIMATED HEATS OF REACTION* (kcal/mole)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAlOH (2A') → AlOH (¹Σ⁺) + H (²S)</td>
<td>+52</td>
</tr>
<tr>
<td>HAlOH (2A') → AlO (²Σ⁺) + H₂ (¹Σ⁺)</td>
<td>+59</td>
</tr>
<tr>
<td>HGaOH (2A') → GaOH (¹Σ⁺) + H (²S)</td>
<td>+50</td>
</tr>
<tr>
<td>HGaOH (2A') → GaO (²Σ⁺) + H₂ (¹Σ⁺)</td>
<td>+60</td>
</tr>
<tr>
<td>HInOH (2A') → InOH (¹Σ⁺) + H (²S)</td>
<td>+49</td>
</tr>
<tr>
<td>HInOH (2A') → InO (²Σ⁺) + H₂ (¹Σ⁺)</td>
<td>+59</td>
</tr>
</tbody>
</table>

*Heats of reaction were estimated using bond energy data from references 12, 28, and 29. Promontional energies were estimated by taking the difference in bond energies for M-OH and M-(OH)₂.
light is also sufficiently energetic to activate the homogeneous predissociative channel to form A10.

Electronic transitions from the minimum of the $^2A'$ ground state potential well to the potential minimum of the $^2A''$ excited state requires less than 1.5 eV of energy; therefore, to supply the energy required for the endothermic photoreactions to form A10 (2.5 eV; 3.2 eV) and A10H (2.2 eV), the electronic transition from the $^2A'$ ground state of H10H must access very high vibrational levels in its $^2A''$ first excited state. As previously stated, the $^2A''$ and $^2A'$ electronic states are most likely derived from a Renner-Teller distortion of a linear $^2\Pi$ state which implies a large change in conformation between the $^2A'$ and $^2A''$ states if the interaction is sufficiently strong /20/. A dramatic geometric difference between the two states generates large off-diagonal Franck-Condon factors for the $^2A'' + ^2A'$ transition. Therefore, the electronic transition should be able to access the high vibrational levels in the $^2A''$ excited state necessary for the endothermic predissociative photochemistry.

It would be very interesting to study in a more detailed fashion the onset wavelengths required to initiate heterogeneous predissociation to form A10H and A10 and the homogeneous predissociation to form A10 by employing
a tunable laser as the photolysis source. Since branching
to form two pairs of products from HA10H is observed, it
may be possible to select wavelengths of light that
selectively generate one particular product pair to the
exclusion of the other pair of products. Certainly a
more detailed understanding of the potential energy
surfaces involved in the photochemistry would be gleaned
from such an investigation.

It is striking to note that the infrared investiga-
tion of the aluminum-water chemistry did not observe the
formation of A10 upon irradiation of HA10H with 3000 \AA
photons yet this work reports a very good yield of A10
for the identical photolysis study. The only distinguish-
ing feature between these two studies is that the IR
studies utilized argon for the matrix medium whereas the
U.V.-VIS work employed krypton as the host. In the gas
phase, Oblath and Gole /4/ have studied the oxidative
interaction of aluminum and water vapors observing
emission from the $B^2\Sigma^+$ state of A10 during the multiple
collision studies; however, no emission for A10 was
displayed during the single collision studies which
indicates that A10 is probably formed in its ground or
$A^2\Pi$ state by reaction of aluminum with water. They
believe that the HA10H* ($^2A^\prime\prime$) species collisionally
activates the $B^2\Sigma^+$ state of A10 during the multiple
collision studies. Emission from the $A^2\Pi$ state of AlO was not investigated.

Examination of Figures IV-9 and IV-10 indicates that there is no potential energy barrier to the formation of HAlOH ($^2A'$) from a recombination of AlO ($^2\Sigma^+$) and H$_2$ ($^1\Sigma_g^+$); however, there is a barrier to recombination of ALOH ($^1\Sigma^+$) and H ($^2S_g$) to reform HAlOH ($^2A'$). So rapid separation of the AlO + H$_2$ products as they dissociate may be necessary to stabilize them with respect to recombination. This rapid separation can readily be achieved in the gas phase, but in the rare gas solid matrix, the matrix cage enclosure will certainly hinder product separation especially if there is a mechanism for efficient nuclear kinetic energy quenching of the products by the rare gas solid.

Since photodissociation occurs on a $10^{-14}$ second time scale, the rare gas solvent does not have time to resolvate the guest species in dissociation. The host interaction is effectively locked into the ground state configuration. So instead of the dissociating fragments colliding with the lattice of coupled rare gas atoms, the fragments impulsively collide with the nearest neighbor rare gas atom. Transfer of nuclear kinetic energy is more efficient for fragments that have mass values near that of the rare gas host atom. Since the mass of the
AlO molecule is very near to that of the Ar atom, thereby permitting very efficient nuclear kinetic energy transfer from AlO to Ar, it is reasonable to believe that the probability for recombination of AlO and H\textsubscript{2} to form HAlOH is greatly enhanced since these fragments do not have the opportunity to depart from the host matrix cage. On the basis of this tentative argument one would not expect efficient formation of AlO in an argon matrix; however, AlO formation would be predicted in a krypton matrix because of the disparity in masses between AlO and Kr. In both the argon and krypton host mediums, the HAlOH product yield should not be hindered because of the barrier to recombination.

2. **GALLIUM-INDIUM AND WATER**

   a. **NATURE OF THE ELECTRONIC TRANSITION OF THE METAL-WATER COMPLEX**

   Unlike aluminum, the gallium and indium metal atoms did not spontaneously insert into the O-H bond; rather, they formed a complex with water with the metal coordination to the 3a\textsubscript{1} lone electron pair on the oxygen atom in the plane of the water molecule. Hydrate or adduct formation perturbs the electronic structure of Ga and In such that the \( ^2S + ^2P \) atomic transition for the metal when complexed with water is significantly broadened and red shifted from the uncomplexed atomic resonance tran-
sition. Insight to the nature of the perturbation that leads to red shifted spectra may be gleaned from an examination of Figure IV-11 which shows the metal in its ground and excited states approaching the water molecule from infinite separation. At suitable metal-water separations, the metal atom is unperturbed by the water molecule, and a normal atomic resonance transition is observed which is shown to be of energy $E_2$. As the metal approaches the water molecule in closer proximity, an attractive interaction is encountered such that the equilibrium arrangement finds the metal-water complex bound in a potential energy well. For reasons that will be developed shortly, the water is more highly attracted to the metal in its excited state than its ground state with the result that the potential energy well depth in the excited state, $\varepsilon^*$, is greater than that of the ground state, $\varepsilon$. Consequently, the energy of the $A \rightarrow X$ metal-water complex transition, $E_1$, is less than that of the atomic resonance transition, $E_2$, thereby generating red shifted spectra for the adduct relative to the atomic resonance lines. The energy difference between $E_1$ and $E_2$ corresponds to a value of stabilization enhancement in going from the ground to the excited state of the complex. If the ground state is very weakly bound, the value represents a measure of the minimum dissociation energy for the excited state
FIGURE IV-11

SCHEMATIC DIAGRAM OF THE POTENTIAL ENERGY SURFACES OF THE METAL-WATER INTERACTION WITH THE METAL IN ITS GROUND AND EXCITED STATES
**TABLE IV-6**

DISSOCIATION ENERGY ESTIMATES\(^a\) FOR THE GROUP IIIA METAL-WATER COMPLEX EXCITED STATE IN SOLID KRYPTON

<table>
<thead>
<tr>
<th>Molecule</th>
<th>State</th>
<th>(2^3S + 2^3P)^d</th>
<th>(E'_{oo})^b,c</th>
<th>(D'_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga···OH(_2)</td>
<td>(2^2A_1)</td>
<td>27.179</td>
<td>20.480</td>
<td>6.700 + (D'_0)</td>
</tr>
<tr>
<td>In···OH(_2)</td>
<td>(2^2A_1)</td>
<td>25.811</td>
<td>19.650</td>
<td>6.160 + (D'_0)</td>
</tr>
</tbody>
</table>

\(^a\) For \((M···OH\(_2\))^*\) dissociating to \(M^*(2^3S) + H_2\O\ (1^2A_1)^*\).

\(^b\) \(\text{cm}^{-1}\).

\(^c\) Estimated from red cutoff of absorption band and the red shoulder on the major adduct band is not used in deriving the red cutoff.

\(^d\) For multiple bands, energy values are taken from the major band position.
potential energy well dissociating to $M^* (2^2S) + H_2O (1^1A_1)$. Such species that are weakly bound in the ground state but fairly well bound in the excited state are categorized as exciplexes.

The energy values for stabilization enhancement for the gallium- and indium-water complexes are 19 and 17.5 kcal/mole, respectively (see Table IV-6). These energy values are in good qualitative agreement with a large number of quantum-chemical calculations that have yielded the dissociation energies for metal-water complexes in their ground and excited states for a variety of metal atoms. The results of these calculations are summarized in Table I-1. For example, the difference in dissociation energies between the $2^2A_1$ adduct ground state and the $2^2B_2$ excited state is about 10 to 14 kcal/mole for the lithium-water complex. In the case of the beryllium-water complex, the energy difference is about 18 kcal/mole. Although these ab initio studies concerned metals from different chemical groups than studied in this work, the qualitative agreement is interesting; however, the nature of the bonding interaction is probably not the same.

The gallium-water and indium-water complexes have three low-lying electronic states corresponding to the water molecule splitting the p orbital degeneracy in the $C_{2v}$ point group. The three electronic states generated
by water's perturbation are $^2B_2$, $^2B_1$, and $^2A_1$ corresponding to the unpaired electron residing in the $b_2$-$p_y$, the $b_1$-$p_x$, or the $a_1$-$p_z$ orbital, respectively. Reference to Figure IV-12 is helpful in understanding the nature of these low-lying electronic states for the complex. This figure diagrams the atomic and molecular orbitals for gallium and water as they approach each other to form the complex constrained within the $C_{2v}$ point group. If the unpaired electron occupies the $a_1$-$p_z$ orbital, it will directly confront the electron density in the $3a_1$ lone pair on water so the $^2A_1$ state is probably not stable due to the electron-electron repulsion. Ab initio results in fact do indicate that the $^2A_1$ state for $(\text{Li} \cdots \text{OH}_2)^*$ is repulsive. Both the $^2B_2$ and $^2B_1$ states are expected to be attractive since these states correspond to an orbital occupancy that disperses the unpaired electron density away from the nucleus so the $3a_1$ lone pair on water may encounter an enhanced electrostatic attraction. The ab initio results for $(\text{Li} \cdots \text{OH}_2)^*$ also indicate that the $^2B_2$ and the $^2B_1$ states are attractive. The calculations also indicate that the $^2B_2$ state is more stable than the $^2B_1$ state because the occupation of the $b_2$-$p_y$ orbital makes possible a favorable quadrupole-quadrupole interaction between the water molecule's overall quadrupole along the $y$-axis in the $y$-$z$ plane and the metal's $b_2$-$p_y$
FIGURE IV-12

MOLECULAR AND ATOMIC ORBITAL ENERGY DIAGRAM
FOR THE GALLIUM–WATER INTERACTION
orbital quadrupole. The occupation of the $b_1$-$p_x$ orbital generates a repulsive quadrupole-quadrupole interaction between the water's $b_1$ orbital quadrupole and the metal's $b_1$-$p_x$ orbital quadrupole. Thus, the electronic ground state of the gallium-water complex is most likely $^2B_2$ due to a favorable Coulombic interaction that is unfavorable in the $^2B_1$ state.

The A + X transition for the complex involves promotion of the unpaired electron to the $a_1$-5s orbital on the metal which generates an unequivocal $^2A_1$ electronic state since the $a_1$-5s orbital is not degenerate. Thus, the observed A + X transition for the gallium- and indium-water complexes may be identified with a $^2A_1 + ^2B_2$ symmetry allowed electronic transition that corresponds to an electron configuration rearrangement of . . . $(3a_1)^2(2b_2) + . . . (3a_1)^2(5a_1)^{-1}p_y + 5s$ for the Ga-H$_2$O complex.

It is fruitful to examine Figure IV-12 in discussing the nature of the bonding in the excited state of the gallium- and indium-water complexes. In studying the interaction of the metal-water complex, Bentley /21/ states that the principal noncovalent attractive force between the metal and the water is electrostatic in origin with minor polarization and charge-transfer components. This result is consistent with the interpretation that
the metal-water bonding arises from an electrostatic attraction between the metal's nucleus and water's $3a_1$ lone electron pair. In the case of the Group IA and IIA metal atom-water molecule interactions, an electronic transition involves delocalization of electron density on the metal by vacating the $a_1$-4s orbital and occupation of the $b_2$-$p_y$ orbital which enhances the electrostatic attraction between water's $3a_1$ lone pair and the nucleus of the metal by generating a positive σ hole on the metal. However, the Group IIIA metal-water complex electronic transition involves vacating a $b_2$-$p_y$ orbital and occupation of the $a_1$-5s orbital. There is some delocalization of electron density in this case which can enhance the electrostatic attraction in the excited state; however, additional stabilization in the excited state may be derived if the singly occupied $a_1$-5s orbital mixes with the $4a_1$ antibonding orbital of water. The $4a_1$ orbital is the highest occupied molecular orbital in the water anion /22/; consequently, a mixing of these two orbitals implies a mixing of the $M^+ \cdots OH^- \cdot 2A_1$ charge-transfer state with the $2A_1$ adduct excited state resulting in a destabilization of the charge-transfer state and a stabilization of the $2A_1$ adduct excited state. The previous discussion is more lucidly depicted in Figure IV-13 which is a state correlation diagram showing the
approach of Ga toward water in a $C_{2v}$ frame of reference. Ga$^+$ ($^1S$) and $H_2O^-$ ($^2A_1$) form the $^2A_1$ charge-transfer state that is destabilized upon adduct formation to the benefit of the $^2A_1$ state derived from Ga ($^2S$) and $H_2O$ ($^1A_1$). Therefore, one might predict that the charge-transfer forces are of more consequence in the overall bonding interaction in the $^2A_1$ excited state than the $^2B_2$ ground state for the gallium- and indium-water complexes.

b. ORBITAL AND STATE CORRELATIONS

Figures IV-13 and IV-14 show the state correlation diagrams for the gallium- and indium-water chemical interactions. These correlation diagrams are very similar to the aluminum-water state diagram. In the $C_s$ approach of the metal toward the water, the $M$ ($^2P$) + $H_2O$ ($^1A_1$) ground state is split into three electronic states: one $^2A''$ state and two $^2A'$ states. The $^2A''$ state correlates directly into the first $^2A''$ excited state of the HMOH molecule without encountering any surface intersections. The lowest $^2A'$ state of the reactants correlates adiabatically into the $^2A'$ ground state of the HMOH molecule by virtue of an avoided crossing with the charge-transfer potential surface that generates a potential energy barrier to reaction along this $^2A'$ ground state surface. This potential barrier is created because the lowest $^2A'$
FIGURE IV-13

ELECTRONIC STATE CORRELATION DIAGRAM FOR

THE GALLIUM-WATER INTERACTION

... DENOTES REPULSIVE STATES

--- DENOTES STATES WHICH HAVE NOT BEEN OBSERVED

0 DENOTES AN AVOIDED SURFACE INTERSECTION
FIGURE IV-14

ELECTRONIC STATE CORRELATION DIAGRAM

FOR THE INDIUM-WATER INTERACTION

... DENOTES REPULSIVE STATES

--- DENOTES STATES WHICH HAVE NOT BEEN OBSERVED

0 DENOTES AN AVOIDED SURFACE INTERSECTION
reactant state diabatically correlates into the first \(^2A^\prime\) excited state of HMOH which is probably rather high in energy. Table IV-4 indicates that the reaction of gallium inserting into the O-H bond of water is exothermic by about 34 kcal/mole which is almost one-half the amount of energy released in the aluminum insertion reaction. The heat of reaction for the indium insertion reaction is only exothermic by about 17 kcal/mole. Although the \(^2A^\prime\) first excited state of HMOH was not observed spectroscopically in the matrix, the energy of transition may be roughly estimated by assuming the value is close to that of HAlOH's \(^2A^\prime\) \(+\) \(^2A^\prime\) transition. This argument leads to the conclusion that the \(^2A^\prime\) state of HGaOH and HInOH is higher in energy relative to the reactant \(^2A^\prime\) state derived from \(^2P_u\) + \(^1A_1\). Consequently, the reaction of gallium and indium inserting into the O-H bond of water, although suitably exothermic, is not expected to occur for two reasons: (1) direct reaction along the \(^2A^\prime\) ground state surface is hindered by a potential energy barrier generated by an avoided surface crossing also encountered in the aluminum-water insertion reaction, and (2) reaction along the \(^2A^\prime\) excited potential surface is also hindered by a potential energy barrier generated by the endothermicity of the reaction to form HGaOH or HInOH in their \(^2A^\prime\) states which was not encountered in the Al-H\(_2\)O reaction because this process is quite exothermic.
This analysis rationalizes the different chemical behavior observed for these three chemical systems in the IR matrix studies which reported that Al spontaneously inserted into the O-H bond of water whereas Ga and In did not; rather, gallium- and indium-water adducts were initially formed which subsequently could be photolyzed to generate the HGaOH and the HInOH molecules.

At this juncture, it is of interest to try to understand the nature of the photochemical channel that is pursued by the reactant when the gallium and indium metal atom insertion reactions are induced by irradiation of the metal-water complex. To this end, an examination of Figures IV-13 and IV-14 is fruitful. The metal-water complex in the $C_{2v}$ point group has a $^2B_2$ ground state. The first observed excited state of this complex is the $^2A_1$ state derived from M ($^2S$) and $H_2O$ ($^1A_1$). This $^2A_1$ state resolves into a $^2A'$ state if the $C_{2v}$ point group symmetry is broken by the complex rearranging with the metal approaching the O-H bond in the plane of the water molecule which has symmetry corresponding to the $C_s$ point group. The charge-transfer state that diabatically correlates into the $^2A'$ ground state of the HMOH molecule is also of $^2A'$ symmetry so it intersects the complex's $^2A'$ state in an avoided surface crossing thereby permitting it to adiabatically evolve into a lower $^2A'$ state of the HMOH molecule. Since the ionization potential of M ($^2S$)
is only 3.0 eV, and the electron affinity of water \( ^1A_1 \)
is about zero, the surface intersection is expected to
occur very early in the rearrangement of the complex to
form HMOH so the development of a significant potential
barrier is not expected. However, favorable Franck-Condon
factors would probably allow more energetic photons to
access sufficiently high vibrational levels in the \(^2A_1\)
state to overcome any barrier to reaction that may exist.
Therefore, photolyzing the metal-water complex with the
appropriate wavelength of light populates the \(^2A_1\) excited
state of the adduct which is unstable with respect to
rearrangement to form the HMOH molecule in its second
excited \(^2A'\) state where the reactants follow along an
excited \(^2A'\) potential surface. The excited HMOH molecule
may then decay into its \(^2A'\) ground state. To verify and
perhaps further detail this photochemical mechanism, it
would be interesting to study the chemiluminescent
processes that are initiated by photolysis of the metal-
water complex.

c. PHOTODISSOCIATION OF HGaOH AND HInOH

The observation that bands attributable to the HMOH
molecule could not be assigned in the matrix isolation
spectra may be understood in the context of a qualitative
molecular orbital argument involving orbital correlations
for the linear and bent conformations of HAB (see Figure
IV-5). The HAB molecule models the insertion product where the OH fragment is identified with the B atom, and the metal atom is identified with the A atom. In accord with perturbation theory, the greater the difference in electronegativity between the A and B atoms, the greater the disparity of p orbital contribution to the 5a' - 1π_x MO and the 7a' - 2π_x MO from A and B such that for a very large difference in electronegativity (X_B >> X_A), the 7a' MO is primarily A's p_x orbital, and the 5a' MO is primarily B's p_x orbital. A larger p AO contribution from A to 7a' favors a smaller HAB bond angle since there is an improved AO overlap /17/. Since gallium and indium have a greater electronegativity than aluminum, the electronegativity difference is smaller for the HGaOH and HInOH molecules compared to HAlOH thereby generating a smaller bond angle change in going to the 2_A'' excited state of the linear HMOH* species. This favors the absorption of lower energy light and a smaller bending mode progression since the diagonal Franck-Condon factors are larger in magnitude. Therefore, the 2_A'' + 2_A' transition for HGaOH and HInOH may be beyond the long wavelength limit of the U.V.-VIS spectrophotometer since the 2_A'' (v_2=0) + 2_A' (v_2=0) electronic transition for HAlOH is less than 12,500 cm^{-1}. This transition for HAlOH is observed only by virtue of large off-diagonal
Franck-Condon factors which the $^2A'' + ^2A'$ transition for 
HGaOH and HInOH probably does not have.

Irradiation of the HGaOH and HInOH molecules only 
generates the metal hydroxide product. The correlations 
for these photodissociations are expected to be very 
similar to those correlations constructed for the HALOH 
molecule predissociating to form ALOH + H and ALO + H$_2$ 
(see Figures IV-9 and IV-10). Table IV-5 shows that the 
heats of reaction for the HALOH, HGaOH, and HInOH reactions 
to form the metal hydroxide and metal monoxide are all 
very similar with the MOH ($^1\Sigma^+$) + H$_2$ ($^1\Sigma^+_g$) $^2A'$ product 
ground state being about 21,000 cm$^{-1}$ above the HMOH $^2A'$ 
ground state. The $^2A''$ state of HGaOH and HInOH can 
heterogeneously predissociate into the $^2A'$ ground state 
of the GaOH and InOH products by interaction with the 
out-of-plane torsional mode of HMOH. There is a potential 
energy barrier to recombination generated by an avoided 
surface intersection which stabilizes the metal hydroxide 
product; however, as before, there is not a potential 
barrier to recombination of the MO + H$_2$ products. Since 
there is no barrier, it would be difficult to stabilize 
the metal oxide especially for the heavier metal monoxides 
which due to their larger size may encounter difficulty 
in escaping the matrix cage thereby enhancing recombination 
processes. The smaller argon cage site may also inhibit
AlO formation from HAlOH photodissociation in the infrared investigation of the aluminum-water chemistry.

3. ELECTRONIC STRUCTURE OF THE GROUP IIIA METAL DIMERS

The gas phase emission systems observed from a King furnace for the Group IIIA metal dimers /24,26/ could not be correlated with any of the electronic transitions observed in absorption in the matrix phase for the same dimeric species; however, certain trends were observed. Matrix isolation electronic absorption spectra revealed that two bands could be assigned to each metal dimer (Al₂, Ga₂, and In₂): one band was always in the red region of the spectrum ranging from 13,000 cm⁻¹ to 15,600 cm⁻¹, and the other band was always located in the deep blue region of the spectrum ranging from 24,000 cm⁻¹ to 30,000 cm⁻¹. Only one gas phase emission system was observed for each of these metal dimers all three of which were centered around 18,000 cm⁻¹ ranging from 17,200 cm⁻¹ to 20,000 cm⁻¹. There is agreement between the matrix and gas phase absorption spectra for In₂ since the gas phase absorption spectra also observed a band around 27,000 cm⁻¹. Since the spectral features observed in absorption and emission for each of the metal dimers are quite similar, it is probably true that their electronic structures are also very similar. Therefore statements regarding the
electronic structure of the aluminum dimer may tentatively be extrapolated to have application in describing the electronic structures of the gallium and indium dimers.

The 14,000 cm\(^{-1}\) A – X system and the 24,500 cm\(^{-1}\) B – X system observed in absorption for Al\(_2\) possibly could not be detected in emission from the King furnace because the Al\(_2\) gas phase study /24/ photographed the spectral bands with Kodak IIa-D film which has an operational sensitivity to wavelengths of light between 460 nm (21,700 cm\(^{-1}\)) and 620 nm (16,000 cm\(^{-1}\)). However, the B – X system is so close to the \(^2S - ^2P\) atomic line at 24,788 cm\(^{-1}\) that it is also possible strong emission from Al may have bleached the film in this particular spectral region making it very difficult to perceive the weaker B-X band system for Al\(_2\). The gallium and indium dimer study /26/ photographed emissions from the King furnace with Kodak 103a-F film that has a 450 nm (22,200 cm\(^{-1}\)) to 680 nm (14,700 cm\(^{-1}\)) operational spectral sensitivity which leads one to believe that this study was blind to the B – X system for Ga\(_2\) and In\(_2\) as well as the A – X system for In\(_2\), but the A – X system for Ga\(_2\) should have been photographed. However, as will be discussed, an analysis of the nature of the A state indicates that the A + X emission system may be significantly red shifted from the absorption band due to large off-axis Franck-Condon factors making the emission system impossible to photograph with the film employed.
It is also possible that the B - X system for Ga₂ and In₂ may not have been observed in emission because the B states could not be thermally populated at the lower operating temperatures required to vaporize Ga and In. Therefore, the band systems observed in matrix absorption for these metal dimers probably could not be discerned in emission out of a King furnace because there was a mismatch between the film spectral response and the energies of the A - X systems and possibly the B - X systems; interfering atomic emission and inability to thermally populate the B state would also rationalize the failure to observe the B - X systems.

Since the gas phase Al₂ 3Σ⁻ u → 3Σ⁻ g emission system was not observed in absorption in the matrix, the identification of the lower 3Σ⁻ g state in emission to the ground state is incorrect, and thus the proper assignment for the ground state of Al₂ is open to question. Ginter and Innes /24/ report that the lower 3Σ⁻ g state corresponds to an electron configuration of

$$KKLL(σ_g 3s)^2(σ_u 3s)^2(π_u 3p)^2$$

which can arise from two ground state 2P_u aluminum atoms. They expect the upper 3Σ⁺ u state to correspond to a

$$KKLL(σ_g 3s)^2(σ_u 3s)(π_u 3p)^2(σ_g 3p)$$
electron configuration that probably arises from $^2P_u + ^4P_g$
atoms. The electron configuration given for the $^3\Sigma_g^-$ state
is undoubtedly correct since it is the only low energy
orbital occupation that gives rise to a $^3\Sigma$ state. Besides
the $^3\Sigma_g^-$ state, $^1\Delta_g$ and $^1\Pi_g$ states may also arise from the
$(\sigma_g)^2(\sigma_u)^2(\pi_u)^2$ electron configuration. However, these
states are predictably higher in energy than the observed
$^3\Sigma_g^-$ state due to spin pairing to form the singlet; so the
orbital occupancy of the ground state must be different
from that given above. There are only two other possible
low energy electron configurations:

$$(1) \text{KKLL}(\sigma_g3s)^2(\sigma_u3s)^2(\sigma_g3p)^2-^1\Sigma_g^+$$

and

$$(2) \text{KKLL}(\sigma_g3s)^2(\sigma_u3s)^2(\sigma_g3p)(\pi_u3p)^2-^3\Pi_u$$

Electron configuration (2) would arise only if the energy
of separation of the $\sigma_g3p$ and $\pi_u3p$ orbitals is less than
the spin pairing energy involved in placing two electrons
in the $\sigma_g3p$ orbital. Both electron configurations can
arise from two ground state $^2P_u$ aluminum atoms.

Graham and Weltner /27/ have observed the 3200 Å
Douglas-Herzberg $3\Gamma_u^--3\Gamma_g^-$ system for $B_2$ in a solid argon
matrix in absorption thereby substantiating that the
ground state of $B_2$ is $^3\Sigma_g^-$ with the following electron
configuration:
\[ \text{KK}(\sigma_g)^2(\sigma_u)^2(\pi_u)^2 \]

In comparing this configuration for \( B_2 \) with the two configurations proposed for \( \text{Al}_2 \), it is apparent that in going from \( B_2 \) to \( \text{Al}_2 \), the \( \sigma_g3p \) orbital lowers in energy below the previous \( \pi_u3p \) HOMO making the \( \pi_u3p \) the LUMO. An identical molecular orbital energy reversal is observed in going from \( C_2 \), which has a \( \Sigma^+ \) ground state, to \( \text{Si}_2 \), which has a \( 3\Sigma^- \) ground state. This orbital reversal can occur if s-p mixing becomes less significant and/or if \( \pi \) bonding becomes weaker. If the energy difference between the \( \sigma_g3p \) and \( \pi_u3p \) orbitals continues to increase in going down the Group IIIA column from \( \text{Al}_2 \) to \( \text{In}_2 \), as one might expect from the \( B_2 \rightarrow \text{Al}_2 \) trend, the ground state of \( \text{In}_2 \) is predictably \( 1\Sigma^+ \) since the energy of orbital separation would destabilize the \( 3\Pi_u \) state. Since the empirical electronic structure observed in absorption and emission for the three metal dimers is very similar, the assignments for the transition systems are probably identical for each metal dimer which implies a \( 1\Sigma^+ \) ground state assignment for \( \text{Ga}_2 \) and \( \text{Al}_2 \).

\textit{Ab initio} calculations on \( \text{Al}_2 \) by Leleyter and Joyes /25/ utilizing SCF-CI methods find that the \( 1\Sigma^+ \) state is only 2500 cm\(^{-1}\) above the \( 3\Sigma^- \) state.

Molecular orbital theory is of assistance in establishing the natures of the A and B states observed in absorption in the matrix. The A state can not arise
from \( ^2P_u + ^4P_g \) atoms since this combination gives rise to states with triplet and quintet multiplicities that can not be accessed in an allowed fashion from a singlet ground state. The A state probably does not arise from \( ^2S_g + ^2P_u \) atoms since this combination gives rise to highly excited electron configurations that are difficult to associate to this low energy transition. In fact, such an association would imply that the excited A state is significantly more bound than the ground state which is not reasonable. By elimination, therefore, the A state in all probability arises from two ground state \( ^2P_g \) aluminum atoms. Of the myriad of states that arise from this combination /30/, spin and parity selection rules eliminate all but two: the \(^1\Sigma_u^-\) and the \(^1\Pi_u\) states. However, the \(^1\Sigma_u^-\) state is an improbable choice for A since it implies a simultaneous two electron promotion in the electron configuration for the \( A + X \) transition and is electric-dipole forbidden. Thus, from this analysis, the \( A + X \) transition can be tentatively assigned to a \(^1\Pi_u + ^1\Sigma_g^+\) transition. The \(^1\Pi_u\) state corresponds to a

\[
KKLL(\sigma_g 3s)^2(\sigma_u 3s)^2(\sigma_g 3p)(\pi_u 3p)
\]
electron configuration for \( Al_2 \) which is probably bound in character since it corresponds to a formal bond order of a little better than one-half.
It is interesting to note that the energy of transition, about 14,000 cm$^{-1}$, is greater than the energy of dissociation for the ground state, about 12,000 cm$^{-1}$. The electronic transition from the $1\Sigma^+_g$ ground state must then access the repulsive portion of the $1\Pi_u$ potential energy surface since the $1\Pi_u$ state is bound and arises from two ground state $2P_u$ aluminum atoms. This implies a large difference in the internuclear distance between the ground and excited states which is expected since the ground state has a formal bond order of one. Transitions from bound states to repulsive surfaces generate broad continuous spectra which is consistent with the very broad, structureless bands observed for the $A(1\Pi_u) + X(1\Sigma^+_g)$ transitions of $\text{Al}_2$, $\text{Ga}_2$, and $\text{In}_2$ in absorption in the matrix spectra.

The B state observed in absorption can not arise from a $2P_u + 4P_g$ atom combination for the same reasons previously mentioned; rather, it probably arises from $2P_u + 2S_g$ aluminum atoms. Of the various states that arise from this combination, the state that is lowest in energy that involves an allowed transition from the ground state is the $1\Sigma^+_u$ state that corresponds to a

$$KKLL(\sigma_g3s)^2(\sigma_u3s)^2(\sigma_g3p)(\sigma_u4s)$$

orbital occupancy for $\text{Al}_2$. Therefore, the short wavelength electronic absorption observed in the matrix for $\text{Al}_2$, $\text{Ga}_2$,
and In$_2$ is tentatively assigned to a $A(^1\Sigma_u^+) \rightarrow X(^1\Sigma_g^+)$ transition.
REFERENCES


CHAPTER FIVE

ELECTRONIC MATRIX ISOLATION SPECTROSCOPIC STUDIES
OF THE GROUP IVA METAL–WATER PHOTOCHEMISTRY
CHAPTER FIVE

OUTLINE

V. ELECTRONIC MATRIX ISOLATION SPECTROSCOPIC STUDIES OF THE GROUP IVA METAL–WATER PHOTOCHEMISTRY

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V. ELECTRONIC MATRIX ISOLATION SPECTROSCOPIC STUDIES OF
THE GROUP IVA METAL-WATER PHOTOCHEMISTRY

A. INTRODUCTION

There have been several previous experimental and
theoretical investigations of the Group IVA metal atom
hydration interactions and reactions. Kauffman /4/ has
performed infrared matrix isolation studies of the inter-
actions of Group IVA metal atoms with water molecules in
argon matrices at 15 K. These studies demonstrated that
initially upon cocondensation of the metal and water vapor,
the metal atoms form a 1:1 complex with water molecules as
evidenced by a decrease in the \( \nu_2 \) bending mode frequency of
water. The \( \Delta \nu_2 \) decrease upon adduct formation ranged from
-18.6 cm\(^{-1}\) for Si to -8.0 cm\(^{-1}\) for Pb; the Ge and Sn adducts
had intermediate values for \( \Delta \nu_2 \). Since the red shift has
been successfully used as a semiquantitative probe of the
strength of interaction between the metal and water, these
results indicate a steady decrease in the M\(\cdots\)O attraction
going down the periodic table from Si to Pb. The Si\(\cdots\)OH\(_2\)
adduct displayed a curious behavior in that it spontaneously
rearranged in total darkness over a relatively short period
of time (several hours) to form the oxidative insertion
product, HSiOH; however, the Si\(\cdots\)OD\(_2\) adduct was not observed
to be reactive in this regard. Ismail and coworkers /5/ have investigated the kinetics of this adduct rearrangement at different temperatures. Since they noted no change in the reaction rate upon a moderate elevation of the matrix temperature, the behavior couldn't be interpreted in terms of a classical isotope effect. Consequently, they concluded that a hydrogen tunneling mechanism was the more plausible rationalization for the observed Si-H_{2}O adduct rearrangement behavior. The infrared studies /4/ also demonstrated that irradiation of the metal-water complex with short wavelength light induced the metal to insert into the O-H bond of water for all the Group IVA metals studied except lead which remained complexed with water after photolysis. Continued photolysis of the matrix caused the HMOH molecule (M = Si, Ge, and Sn) to photo-dissociate and form the metal monoxide and molecular hydrogen. The metal analogues of formaldehyde, H_{2}MO where M = Si, Ge, Sn, and Pb, were not observed except, possibly, for silicon where Kauffman /4/ assigned several infrared bands to H_{x}SiO where x = 1 or 2.

There have been relatively few theoretical calculations performed on the Group IVA metal-water interactions. Bentley /6/ has calculated the C···OH_{2} adduct to be bound by 2.9 kcal/mole in the \(^3A_2\) state. He also reported that the low-lying \(^1A_1\) excited states corresponding to orbital
occupations of $2s^22p^2(a_1^2b_1^2)$ and $2s^22p^2(a_1^2b_2^2)$ are likely to be bound. Pople /7/ has calculated activation energies required for molecular rearrangements of $H_2CO$ to $HCOH$ (trans) and $HCOH$ (trans) to $HCOH$ (cis) to be 86.2 kcal/mole and 28.6 kcal/mole, respectively. Jordan and Sakai /16/ have conducted SCF calculations investigating the equivalent bond distances and angles of $HSiOH$. The results of their calculations indicated that the trans isomer may be slightly more stable.

In view of these previous experimental and theoretical investigations of the Group IVA metal hydration interactions, it is of interest to study the electronic structures of the Group IVA metal atom interactions and reactions with water isolated in rare gas matrices at cryogenic temperatures. Such an investigation may be of assistance in (1) elucidating the nature of the photochemical exit channels pursued by the metal-water complexes in rearranging to form the $HMOH$ molecule, as well as (2) characterizing the electronic structure of the metal-water exciplex thereby providing a data bank to which future theoretical calculations may compare. This study will also serve as a useful adjunct to the previous infrared matrix isolation studies, in that it will examine the perturbations of the electronic structure of metal atoms upon interaction with water. Molecular orbital and electronic state-to-state correlation
diagrams will be employed to help understand the photolytically induced reaction pathways. Additionally, band assignments for the Ge₂ molecular species will be presented.

B. EXPERIMENTAL

Silicon, germanium, and lead metals were procured from MCB, A.D. MacKay, and Fisher, respectively, and were at least 99.5% pure. Tin was available from a laboratory supply and was 99%+ pure. The silicon and germanium metals were vaporized from high density graphite crucibles, whereas the tin and lead metals were vaporized from alumina crucibles. The temperatures of the high density graphite crucibles were monitored with an optical pyrometer for the silicon and germanium metal systems and will be reported for each experiment. During deposition, the oven temperatures corresponded to vapor pressures of the metal employed of $1 \times 10^{-4}$ to $1 \times 10^{-3}$ mm Hg. When tin and lead were being studied, the furnace-crucible assembly was outgassed for two hours prior to deposition at a temperature that corresponded to $10^{-4}$ mm Hg for the metal employed. However, in several experiments involving the vaporization of silicon and germanium, the furnace-carbon crucible assembly was outgassed 10 to 48 hours prior to deposition at temperatures near those used during the actual deposition of the metals. The extent of outgassing will be reported for each of the silicon and germanium experiments.
Extensive outgassing was necessary to liberate extraneous carbon monoxide residing in the high density graphite cell and to lower the concentration of molecular hydrogen in the matrix whose presence was perspicuous from the formation of monosilane (SiH₄) and silylene (SiH₂) presumably from the reaction of Si with H₂ /5/. Evidently molecular hydrogen is generated by pyrolytic cracking of the diffusion pump oil impinging on the Ta foil furnace when elevated to the high temperatures required to vaporize silicon and germanium. Hydride formation was not troublesome apparently when vaporizing tin and lead. To alleviate the radiant heat loads on the Pyrex vacuum vessel from the furnace assembly, secondary and tertiary heat shields comprised of one-mil Ta foil were positioned around the furnace assembly. Host-to-guest ratios in the matrices were measured with the quartz crystal microbalance and will be reported for each experiment. Each matrix sample required 15 minutes to prepare.

C. RESULTS

1. SILICON AND WATER

Cocondensation of silicon and water vapor on a sapphire substrate maintained at 15 K in an excess of krypton generated a transparent, colorless matrix.
Figure V-1 shows three electronic absorption spectral traces corresponding to three experiments: Si/Kr (extensively outgassed); Si/Kr (moderately outgassed); and Si/H₂O/Kr. Table V-1 lists the assignments corresponding to the band maxima for each of these spectra. The strong broad band denoted by "A" in trace A at 2347 Å (42,599 cm⁻¹) appears to be due to silicon atoms. In the gas phase, silicon has an allowed 3p⁴s(⁳P) + 3p²(⁵P) atomic resonance transition at about 39,800 cm⁻¹. Although no definite assignment can be made, it appears reasonable to assume that band "A" may be assigned to this gas phase transition with a ν_{Kr} - ν_{gas} shift of +2,800 cm⁻¹. In general, atomic transitions are blue shifted from their gas phase values in rare gas matrices /8/, and this is certainly the case here. Weltner and coworkers /9/ have studied the optical spectra of silicon atoms in argon matrices. They assign a strong 43,090 cm⁻¹ band to the 3P⁻⁺3P atomic transition of silicon which is in good agreement with the assignment made here since atomic transitions in krypton matrices should be less blue shifted from the gas phase energy relative to argon matrix transitions. However, they report a strong band at 45,648 cm⁻¹ that is assigned to the 3D⁻⁺3P transition for silicon which is not observed in this study.

Mass spectrometric work by Honig /10/ has established that atomic silicon is the predominate vapor species over molten silicon with Si₂, Si₃, and Si₄ present at about 1
FIGURE V-1

ELECTRONIC ABSORPTION SPECTRA FOR SILICON AND WATER ISOLATED IN A KRYPTON MATRIX

Trace A  --  High density graphite cell outgassed for 14 hours at 1000°С then for two hours at 1350°С. Si:Kr = 1:300; T = 1420°С.

Trace B  --  High density graphite cell outgassed for two hours at 1500°С. Si:Kr = 1:340; T = 1435°С.

Trace C  --  Same as Trace B except doped with water. Si:H₂O:Kr = 1:2:200; T = 1480°С.
TABLE V-1

ASSIGNMENTS FOR THE OPTICAL ABSORPTION SPECTRA
OF THE Si/H₂O/Kr SYSTEM

<table>
<thead>
<tr>
<th>Peak</th>
<th>( \lambda (\text{Å}) )</th>
<th>( \bar{v} ) (^{a, b} )</th>
<th>Species</th>
<th>Assignment (^{f} )</th>
<th>Gas Phase (^{a, g} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2347</td>
<td>42 599</td>
<td>Si</td>
<td>3p4s(3P) + 3p²(3P)</td>
<td>39 800°</td>
</tr>
<tr>
<td>B</td>
<td>2658</td>
<td>37 616</td>
<td>?</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2715</td>
<td>36 838</td>
<td>?</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2772</td>
<td>36 070</td>
<td>?</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2832</td>
<td>35 311</td>
<td>?</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>2979</td>
<td>33 563</td>
<td>SiN₂</td>
<td>B+X(3Σ⁻)</td>
<td>Table V-2</td>
</tr>
<tr>
<td>C</td>
<td>3136</td>
<td>31 892</td>
<td>SiN₂</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>D</td>
<td>3190</td>
<td>31 345</td>
<td>Si₂</td>
<td>K(3Σ⁻) + X(3Σ⁻)</td>
<td>30 769°</td>
</tr>
<tr>
<td>D</td>
<td>3235</td>
<td>30 913</td>
<td>Si₂</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>D</td>
<td>3281</td>
<td>30 476</td>
<td>Si₂</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>E</td>
<td>3338</td>
<td>29 962</td>
<td>SiN₂</td>
<td>A+X(3Σ⁻)</td>
<td>Table V-2</td>
</tr>
<tr>
<td>E</td>
<td>3381</td>
<td>29 578</td>
<td>SiN₂</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>E</td>
<td>3428</td>
<td>29 170</td>
<td>SiN₂</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>E</td>
<td>3481</td>
<td>28 724</td>
<td>SiN₂</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>E</td>
<td>3535</td>
<td>28 291</td>
<td>SiN₂</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>E</td>
<td>3596</td>
<td>27 807</td>
<td>SiN₂</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

\( ^{a} \text{cm}^{-1} \), \(^{b} \pm 15 \text{ cm}^{-1} \), \(^{c} \text{Average of the } 3\text{P}_0,1,2 \text{ states;}
^{d} \nu_{00}; \Delta G'_{3/2} = 451 \text{ cm}^{-1}; \quad ^{e} \Delta G'_{v+1/2} = 435 \text{ cm}^{-1}; \quad ^{f} \text{Energies of transition are taken from band maxima unless noted otherwise;}
^{g} \text{From refs. } 1 \text{ and } 2. \)
to 2%. Consequently, one might expect to isolate small metal aggregates in the matrix during deposition irrespective of the degree of isolation in the rare gas. The $\text{Si}_2$ spectrum is well known in the gas phase /2,11,12/ and in the matrix /2,13,14/. The set of bands denoted by "D" in trace B are assigned to the $\text{K}(^3\Sigma_u^-) + \text{X}(^3\Sigma_g^-)$ band system of $\text{Si}_2$ because of their close correspondence to the previous gas phase and matrix bands. Milligan and Jacox /13/ also reported the observation of the D + X system of $\text{Si}_2$; however, this system could not be deconvoluted in this work since it was overlapped with another stronger, unidentified progression at about 35,300 cm$^{-1}$ with an average spacing of about 770 cm$^{-1}$ (the bands denoted by "B"). During the course of a number of experiments, the intensities of these bands varied independently from the intensities of the other band systems which suggests that these bands uniquely correlate to a particular molecular species. Weltner and coworkers /9/ also observe an unidentified progression in argon matrices that obscured the D + X system of $\text{Si}_2$ but with an average spacing of about 870 cm$^{-1}$. They lightly suggest that the progression may be attributable to the Si-Si-O molecule since the $^1\Pi + ^1\Sigma$ system of SiO was always apparent in their optical spectra. Since SiO was not a contaminant in this work yet the unidentified progression was still observed, identification of the band system with $\text{Si}_2\text{O}$ is dubious.
The "E" band progression and the two "C" bands are assigned to electronic transitions of SiN₂ since the band assignments correlate very well with those made by Weltner /9/ for SiN₂ which he formed by condensing silicon atoms in argon matrices doped with nitrogen. Table V-2 compares the band assignments and spacings of the A + X and B + X systems of SiN₂ for this work and Weltner's work. The vibrational numbering is tentative. The 450 cm⁻¹ progression is presumed to be the Si-N stretching frequency, and the 1671 cm⁻¹ spacing is thought to represent the N-N stretching frequency in the excited state. Weltner suggests associating the A + X system with a $3\pi(3\Pi) + 2\pi(3\Sigma⁻)$ excitation, weakening the N-N bond. The SiN₂ bands varied widely from day-to-day.

Traces A and B of Figure V-1 compare the consequence of having outgassed the furnace-crucible assembly extensively and moderately. Trace A shows a spectrum corresponding to a 14 hour outgassing of the assembly at 1000 °C then two hours at 1350 °C, whereas trace B shows a spectrum corresponding to the assembly outgassed for two hours at 1500 °C. Extended outgassing was apparently successful in eliminating a band at about 41,000 cm⁻¹ to the red of the silicon $3\Pi + 3\Pi$ transition. This band may possibly be attributed to a silicon hydride directly or indirectly (perhaps perturbing the $3\Pi + 3\Pi$ transition) since extended oven
TABLE V-2

SiN₂ ABSORPTION BANDS IN RARE GAS MATRICES

<table>
<thead>
<tr>
<th>ν&quot;c</th>
<th>ν'(cm⁻¹)b</th>
<th>Δν</th>
<th>ν'(cm⁻¹)</th>
<th>Δν</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>A+X System</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td></td>
<td>27 170</td>
<td>430</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>27 600</td>
<td>470</td>
</tr>
<tr>
<td>2</td>
<td>27 807</td>
<td>484</td>
<td>28 070</td>
<td>470</td>
</tr>
<tr>
<td>3</td>
<td>28 291</td>
<td>433</td>
<td>28 540</td>
<td>453</td>
</tr>
<tr>
<td>4</td>
<td>28 724</td>
<td>446</td>
<td>28 993</td>
<td>431</td>
</tr>
<tr>
<td>5</td>
<td>29 170</td>
<td>408</td>
<td>29 424</td>
<td>401</td>
</tr>
<tr>
<td>6</td>
<td>29 578</td>
<td>384</td>
<td>29 825</td>
<td>353</td>
</tr>
<tr>
<td>7</td>
<td>29 962</td>
<td></td>
<td>30 178</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B+X System</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>31 892</td>
<td>1671</td>
<td>32 162</td>
<td>1672</td>
</tr>
<tr>
<td>1</td>
<td>33 563</td>
<td></td>
<td>33 834</td>
<td></td>
</tr>
</tbody>
</table>

a From ref. 3.
b ± 15 cm⁻¹.
c Tentative numbering from ref. 3.
d Krypton matrix at 15K.
e Argon matrix at 4K.
operation seemed to be successful in partially eliminating
the silicon hydride bands in the infrared studies /4/.

Doping the krypton matrix condensed with silicon vapor
with water molecules generated no new bands from 210 nm
to 800 nm as is partially evident from trace C. Baseline
instability was a problem that was manifest when working
with metals having high vaporization temperatures irrespec-
tive of the presence or lack of water doping. Doping the
matrix with D₂O was also carried out with the same negative
result. Short and extended photolysis of the silicon and
water doped matrices with light of λ > 3000 Å was also
unsuccessful in generating new bands or changing any
previously present band structure.

2. GERMANIUM AND WATER

Cocondensation of germanium and water vapors on a
sapphire substrate maintained at 15 K in an excess of
krypton generated a transparent, colorless matrix.

Figure V-2 shows three electronic absorption spectral
traces corresponding to three experiments: Ge/Kr; Ge/H₂O/
Kr; and Ge/H₂O/Kr + hv. Table V-3 lists the assignments
 corresponding to band maxima for each of these spectra.
The strong bands denoted by "A" and "B" in trace A at
2332 Å (42,878 cm⁻¹) and 2429 Å (41,168 cm⁻¹) appear to
be attributable to germanium atoms since these are the
FIGURE V-2
ELECTRONIC ABSORPTION SPECTRA FOR GERMANIUM AND WATER ISOLATED IN A KRYPTON MATRIX WITH PHOTOLYSIS

Trace A -- High density graphite crucible outgassed for two hours at 1000°C. Ge:Kr = 1:1000; T = 1165°C.

Trace B -- High density graphite cell outgassed for 12 hours at 1000°C then for 2 hours at 1350°C. Ge:H₂O:Kr = 1:85:490; T = 1260°C.

Trace C -- Same as Trace B but photolyzed for 15 minutes with light of λ > 3000 Å (Pyrex-water filter).
TABLE V-3
ASSIGNMENTS FOR THE OPTICAL ABSORPTION SPECTRA
OF THE Ge/Kr AND Ge/H2O/Kr SYSTEMS

<table>
<thead>
<tr>
<th>Peak λ(A)</th>
<th>ν a,b</th>
<th>Species</th>
<th>Assignment h</th>
<th>Gas Phase a,g</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 2332</td>
<td>42 878</td>
<td>Ge</td>
<td>4p5s(3P2)+4p2(3P0)</td>
<td>39 118</td>
</tr>
<tr>
<td>B 2429</td>
<td>41 168</td>
<td>Ge</td>
<td>4p5s(3P0,1)+4p2(3P0)</td>
<td>37 577 c</td>
</tr>
<tr>
<td>C 2603</td>
<td>38 422</td>
<td>?</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>D 3265</td>
<td>30 625</td>
<td>?</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>E^d 2884</td>
<td>34 677</td>
<td>Ge⋯OH₂</td>
<td>A(3B₂)+X(3A₂)</td>
<td>?</td>
</tr>
<tr>
<td>E 3141</td>
<td>31 835</td>
<td>Ge⋯OH₂</td>
<td>&quot;</td>
<td>?</td>
</tr>
<tr>
<td>E^e 3402</td>
<td>29 396</td>
<td>Ge⋯OH₂</td>
<td>&quot;</td>
<td>?</td>
</tr>
<tr>
<td>F^f 4097</td>
<td>24 410</td>
<td>Ge₂</td>
<td>A→X</td>
<td>?</td>
</tr>
</tbody>
</table>

a cm⁻¹.
b±15 cm⁻¹.
cAverage of the 3P₀,1 states.
dRed onset of peak.
eBlue cutoff of peak.
fNot shown in the spectra.
gFrom refs. 1 and 2.
hEnergies of transition are taken from band maxima unless noted otherwise.
only bands that correlate well with the gas phase atomic resonance transitions for germanium at 39,118 cm\(^{-1}\) \([4p5s(^3P_{0,1}) + 4p^2(^3P_0)]\) and 37,577 cm\(^{-1}\) \([4p5s(^3P_{0,1}) + 4p^2(^3P_0)]\). Although no definite assignment is possible, it seems reasonable to assume that the "A" and the "B" bands may be assigned to these gas phase transitions with corresponding \(v_{Kr} - v_{gas}\) shifts of +3670 cm\(^{-1}\) and +3950 cm\(^{-1}\), respectively. The gas phase \(^3P_2 - ^3P_{0,1}\) (average of \(P_0\) and \(P_1\)) multiplet separation is 1,540 cm\(^{-1}\) which compares favorably with the matrix separation of 1,710 cm\(^{-1}\). The bands denoted by "C" and "D" in trace A correspond to impurities residing in the rare gas matrix. In analogy with what was stated regarding the impurities in the silicon system, these bands are probably attributable to Ge\(N_2\) and/or germanium hydrides. The infrared studies /4/ of germanium and water also noted significant quantities of impurities which were attributed to germanium hydrides. As was noted for the silicon system, extended oven out-gassing helped to discriminate against the "C" bands. Temperature cycling was effective in sharpening the "C" bands, but the band spacings were quite variant.

Because it grew in as a consequence of increasing the water concentration in the matrix, the band denoted "E" in trace B may be assigned to the reaction product of germanium and water which, in collaboration with
previous infrared studies /4/, may be identified with the 1:1 germanium-water adduct. High water dilution studies failed to reveal any change in the structure of band "E" thereby eliminating the possibility of a higher order metal-water interaction causing the broad character of this band which has a red onset at about 29,400 cm\(^{-1}\) and a blue cutoff at about 34,700 cm\(^{-1}\). Trace B' shows that a 15 minute photolysis with light of \(\lambda \geq 3000 \text{ nm} \) (Pyrex-water filter) was effective in totally eliminating the adduct band without subsequent generation of any new absorption bands between 210 nm to 800 nm. This photolytic behavior further substantiates the assignment of band "E" to the adduct since similar behavior was noted for the adduct during the infrared studies /4/.

A broad structureless band denoted by "F" at 4097 \(\text{cm}^{-1}\) (24,410 cm\(^{-1}\)) is assigned to an A + X electronic transition of the germanium dimer since it is the first band to grow in after the atomic bands upon increasing the Ge concentration in the matrix, and the band growth displays a quadratic dependence on the metal deposition rate.

3. TIN AND WATER

Cocondensation of tin and water vapor on a sapphire substrate at 15 K in an excess of krypton generates a transparent, colorless matrix.
Figure V-3 shows three electronic absorption spectral traces corresponding to three experiments: Sn/Kr; Sn/H₂O/Kr; and Sn/H₂O/Kr + hv. Table V-4 lists assignments corresponding to band maxima for each of these spectra. The bands denoted by "A", "B", "C", and "D" correspond to strongly allowed electronic resonance transitions for the tin metal atom since these are the only bands that persist during the course of high dilution studies of Sn and Kr that exclude water doping. These bands also maintain identical relative intensities during the dilution studies. Although no definite assignment is possible, it seems reasonable to assume that the "A" and "B" bands correspond to the gas phase 5p6s(3P₂) + 5p²(3P₀) atomic resonance transition for Sn at 38,629 cm⁻¹, and the "C" and "D" bands correspond to the 5p6s(3P₀,₁) + 5p²(3P₀) transition at 34,778 cm⁻¹ (average of 3P₀ and 3P₁). This assignment implies that the tin metal atom resides in two different matrix sites corresponding to band pairs of "A" - "B" and "C" - "D". Multiple sites for tin in krypton probably reflect a poor fit for the atom in the lattice due to the atom's larger size /8/. The gas phase 3P₂ - 3P₀,₁ multiplet spacing is 3,851 cm⁻¹ which correlates well with the matrix multiplet splittings of 3,935 cm⁻¹ and 4,150 cm⁻¹. The νKr - νgas shifts are 2,770 cm⁻¹ and 773 cm⁻¹ for the double site splitting of the 3P₂ - 3P₀ transition.
FIGURE V-3
ELECTRONIC ABSORPTION SPECTRA FOR TIN AND WATER ISOLATED IN A KRYPTON MATRIX

Trace A -- Sn:Kr = 1:445

Trace B -- Sn:H₂O:Kr = 1:3.4:161

Trace C -- Same as Trace B except photolyzed for 15 minutes with light of λ ≥ 3000 Å (Pyrex-water filter).
### TABLE V-4

ASSIGNMENTS FOR THE OPTICAL ABSORPTION SPECTRA
OF THE Sn/Kr AND Sn/H₂O/Kr SYSTEMS

<table>
<thead>
<tr>
<th>Peak</th>
<th>λ(Å)</th>
<th>$\tilde{v}$ a,b</th>
<th>Species</th>
<th>Assignment d</th>
<th>Gas Phase e</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2416</td>
<td>41 399</td>
<td>Sn</td>
<td>5p6s(3P₂) + 5p²(3P₀)</td>
<td>38 629</td>
</tr>
<tr>
<td>B</td>
<td>2538</td>
<td>39 402</td>
<td>Sn</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>C</td>
<td>2673</td>
<td>37 404</td>
<td>Sn</td>
<td>5p6s(3P₀,₁) + 5p²(3P₀)</td>
<td>34 778 c</td>
</tr>
<tr>
<td>D</td>
<td>2837</td>
<td>35 253</td>
<td>Sn</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>E</td>
<td>2989</td>
<td>33 458</td>
<td>Sn⋯OH₂</td>
<td>E+X(3A₂)</td>
<td>?</td>
</tr>
<tr>
<td>F</td>
<td>3257</td>
<td>30 702</td>
<td>Sn⋯OH₂</td>
<td>A(3B₂) + X(3A₂)</td>
<td>?</td>
</tr>
</tbody>
</table>

a cm⁻¹.

b Average of the 3P₀,₁ states.

c P₀,₁ states.

d Energies of transition taken from band maxima unless noted otherwise.

e From refs. 1 and 2.
The broad bands denoted by "E" and "F" in trace B may be correlated with the 1:1 reaction product of strontium and water since these bands are the first to grow in as a consequence of having doped the matrix with water and maintain identical relative intensities during water concentration studies. In collaboration with the previous infrared studies, these bands may be associated with electronic transitions of the tin-water adduct, Sn⋯OH₂. Trace B' shows that a 15 minute photolysis with light of \( \lambda \geq 3000 \text{ Å} \) was effective in totally eliminating the adduct bands without subsequent generation of any new absorption bands between 210 nm to 800 nm. A comparison of traces B and B' shows that photolysis is also effective in sharpening and changing the relative intensities of the "A", "B", "C", and "D" bands. This suggests that the atomic resonance transitions were superimposed on previously unperspicuous adduct bands. Another photolysis study not shown here shows that selective irradiation of the "F" band without irradiation of the "E" band is effective in eliminating both the "F" and "E" bands. This suggests that the two bands are not simply matrix sites for the same transition but may be associated with two transitions for the same adduct.
4. LEAD AND WATER

Cocondensation of lead and water vapors on a sapphire substrate maintained at 15 K in an excess of krypton generated transparent, colorless matrices. The spectrum displayed bands at 38,067 cm\(^{-1}\) and 35,858 cm\(^{-1}\) which probably correspond to the \(6p7s(3P_{0,1}) \leftrightarrow 6p^2(3P_0)\) atomic transition for Pb in two different sites. The gas phase transition energy is 35,124 cm\(^{-1}\) (average of the \(3P_0\) and \(3P_1\) states) so the matrix transitions are blue shifted by 2,943 cm\(^{-1}\) and 734 cm\(^{-1}\) if this tentative assignment is correct. Doping the matrix with water was not effective in generating new bands as was observed for the Ge and Sn metal systems. This suggests the water does not significantly perturb the electronic structure of the lead metal atom. This is consistent with the infrared results which reported that lead induced the smallest red shift in the bending mode frequency of water (-8 cm\(^{-1}\)) upon adduct formation which is indicative of a small metal-water interaction.

D. DISCUSSION

1. NATURE OF THE ELECTRONIC STATES OF THE GROUP IVA METAL-WATER COMPLEXES

Silicon, germanium, tin, and lead initially formed a complex with water such that the metal is coordinated to the \(3a_1\) lone electron pair on the oxygen atom of the water molecule. It is reasonable to assume that the Group
IVA metal is symmetrically coordinated in the plane of the water molecule according to the \( C_{2v} \) point group since theoretical and experimental results indicated this is the equilibrium conformation for the Group IA, IIA, and IIIA metal-water adducts. Hydrate or adduct formation perturbs the electronic structure of the metal atom in such a manner that the \( 3P + 3P \) atomic transition is red shifted from its respective uncomplexed resonance transition. The \( 3P + 3P \) transition for tin was apparently split by the perturbation of water, and selective photolysis established that the splitting does not originate from the adduct residing in two different matrix sites. The \( A + X \) metal-water complex transition is believed to be red shifted relative to the atomic line because the metal-water interaction potential energy surface in the excited state is deeper than the potential surface in the ground state interaction. The excited state interaction is more attractive because electronic excitation of the metal-water complex involves the displacement of electron density away from the nucleus of the metal so the \( 3a_1 \) lone electron pair on the water molecule may achieve an enhanced Coulombic attraction with the more electropositive excited metal atom. These considerations are consistent with Bentley's quantum-chemical investigations of the metal-water complex which indicate that the principal noncovalent attractive force
between the metal and the water is electrostatic in origin with minor polarization and charge-transfer components. The minimum dissociation energy of the metal-water complex in its excited A state dissociating to \( M^* + H_2O(1A_1) \) may be estimated from the red shift of the A \( \rightarrow \) X band from the \( 3P + 3P \) atomic transition according to the following equation:

\[
D'_o = E(3P + 3P) - E_{oo}(A \rightarrow X) + D''_o
\]

where \( E_{oo} \) may be estimated from the red cutoff of the adduct band observed in absorption, and the value for \( E(3P + 3P) \) is derived from the peak position of the most intense pertinent atomic band. Table V-5 lists the dissociation energies for the germanium- and tin-water complexes in the \( 3B_2 \) excited state. The very broad absorption band observed for the Ge\( \cdots \)OH\(_2\) adduct may be comprised of several closely spaced excited states, as will be discussed shortly, but the state lowest in energy is predictably a \( 3B_2 \) state that correlates to \( M^*(3P_0) + H_2O(1A_1) \). This reasoning is also thought to apply to the low-energy state of the Sn\( \cdots \)OH\(_2\) adduct. However, the state correlation of the other excited state of the adduct that is higher in energy is not unambiguous in view of the multitude of states generated from spin-orbit coupling which is significant in the ground and excited states of the heavier Group IVA metal atoms.
TABLE V-5
DISSOCIATION ENERGY ESTIMATES\(^a\) FOR THE
GROUP IVA METAL-WATER COMPLEX EXCITED STATES
IN SOLID KRYPTON

<table>
<thead>
<tr>
<th>Molecule</th>
<th>State</th>
<th>(3_p \rightarrow 3_p)</th>
<th>(E_{oo}) (^b,c)</th>
<th>(D_o) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si⋯OD(_2)</td>
<td>(^3)(B_2)</td>
<td>42 599</td>
<td>25 000(^f)</td>
<td>17 600 + (D_o)''</td>
</tr>
<tr>
<td>Ge⋯OH(_2)</td>
<td>(^3)(B_2)</td>
<td>41 168(^d)</td>
<td>29 396</td>
<td>11 772 + (D_o)''</td>
</tr>
<tr>
<td>Sn⋯OH(_2)</td>
<td>(^3)(B_2)</td>
<td>37 404(^d,e)</td>
<td>28 333</td>
<td>9071 + (D_o)''</td>
</tr>
</tbody>
</table>

\(^a\)For \((M⋯OH_2)\) dissociating to \(M^* + H_2O\) \((^1A_1)\).

\(^b\)cm\(^-1\).

\(^c\)Estimated from red cutoff of adduct absorption band.

\(^d\)\(^3\)\(P_0,1 \rightarrow ^3\)\(P_0\) atomic transition.

\(^e\)Energy values taken from major band position.

\(^f\)Estimated from selective photolysis studies in ref. 5.
The valence shell ground state electron configuration for a Group IVA metal atom is ns²np² from which the ³P₉, ¹D₉, and ¹S₉ atomic states are derived. The ³P₉ state is the most stable by about one eV. The metal-water complex, in principle, has quite a few more low energy excited states derivable from the ground state electron configuration of the metal atom corresponding to the water perturbation splitting the p orbital degeneracy of the metal atom in the C₂ᵥ point group. According to this perturbation, a total of nine states may be derived from the ns²np² configuration: three states from the ³P₉ state, five states from the ¹D₉ state, and one state from the ¹S₉ state. Table V-6 lists the molecular orbital occupations corresponding to each of these adduct states. According to this table, the ³P₉ state splits into the ³B₁, ³A₂, and ³B₂ states. Since the ³P₉ state is the ground state of the metal atom, one of these states is predictably the ground state of the adduct. Since the ³B₁ and ³B₂ states correspond to orbital occupations with an electron in the a₁ orbital, these states are not expected to be very stable in that the a₁ orbital overlaps the 3a₁ lone pair orbital on water which is a destabilizing interaction according to the discussions in chapters three and four. Consequently, the ³A₂ state, which corresponds to a valence orbital occupation of (a₁)²(b₁)(b₂), is predictably the
TABLE V-6

MOLECULAR ORBITAL OCCUPATIONS CORRESPONDING TO THE
LOW ENERGY STATES OF THE GROUP IVA METAL–WATER
COMPLEXES

<table>
<thead>
<tr>
<th>b_1</th>
<th>a_1</th>
<th>b_2</th>
<th>Atomic Term</th>
<th>Adduct Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>↑↑</td>
<td></td>
<td></td>
<td>1D_g</td>
<td>1A_1</td>
</tr>
<tr>
<td>↑</td>
<td>↑</td>
<td></td>
<td>3P_g</td>
<td>3B_1</td>
</tr>
<tr>
<td>↑</td>
<td>↓</td>
<td></td>
<td>1D_g</td>
<td>1B_1</td>
</tr>
<tr>
<td>↑</td>
<td>↑</td>
<td></td>
<td>3P_g</td>
<td>3A_2</td>
</tr>
<tr>
<td>↑</td>
<td>↓</td>
<td></td>
<td>1D_g</td>
<td>1A_2</td>
</tr>
<tr>
<td>↑↑</td>
<td></td>
<td></td>
<td>1S_g</td>
<td>1A_1</td>
</tr>
<tr>
<td>↑</td>
<td>↑</td>
<td></td>
<td>3P_g</td>
<td>3B_2</td>
</tr>
<tr>
<td>↑</td>
<td>↓</td>
<td></td>
<td>1D_g</td>
<td>1B_2</td>
</tr>
<tr>
<td>↑↑</td>
<td></td>
<td></td>
<td>1D_g</td>
<td>1A_1</td>
</tr>
</tbody>
</table>
symmetry species for the ground state of the adduct. [If the energy difference between the $b_1$ and $b_2$ orbitals is greater than the spin pairing energy, the $^1A_1$ state derived from the $^1D_g$ atomic state with an orbital occupancy of $(a_1)^2(b_2)^2$ is a more reasonable selection for the ground state species. However, the $b_1 - b_2$ energy separations are probably around 2000 cm$^{-1}$, if the separations are near those observed in the Group IIA metal-water interactions, and spin pairing normally requires much more energy than this.] For the heavier metal-water complexes, spin-orbit coupling becomes significant and splits the $^3A_2$ state into three states: $A_1$, $B_1$, and $B_2$. These states are formulated by deriving the direct product of the symmetry species of the electronic state with the species of the spin functions /15/. The energy ordering of these three states can not be determined from this study.

The $^3P_u$ excited states of the metals correspond to valence electron configurations of ns$^2$np(n+1)s, each of which is split by the water interaction into three orbital configurations: $\ldots(a_1)^2(a_1)(a_1)$, $\ldots(a_1)^2(b_1)(a_1)$, and $\ldots(a_1)^2(b_2)(a_1)$. These orbital occupations correspond to $^3A_1$, $^3B_1$, and $^3B_2$ states, respectively. These occupations are analogous to those studied for the Group IIIA metal-water interactions in chapter four where it was learned that the $^1A_1$ state was expected to be repulsive whereas the $^1B_1$ and $^1B_2$ states were predictably stable with the $^1B_2$ state being lowest in energy due to more favorable quadrupole interactions.
Consequently, the $^3B_2$ and $^3B_1$ states are probably stable with the $^3B_2$ state being lowest in energy. Again, for the heavier Group IVA metal-water complexes, spin-orbit coupling plays a more important role potentially splitting the $^3B_2$ state into three states: $A_1$, $A_2$, and $B_1$. The ordering may not be determined from these investigations. Therefore, ignoring the consequences of large spin-orbit coupling, one would expect to observe electronic transitions for the Group IVA metal-water adduct corresponding to $^3B_2 \leftrightarrow ^3A_2$ and $^3B_1 \leftrightarrow ^3A_2$ which are electric-dipole allowed transitions.

The silicon-water adduct did not display any perspicuous band structure in absorption; however, Ismail and coworkers /5/ conducted selective photolysis studies on the Si-D$_2$O system by employing Corning cutoff filters. They reported that light of $\lambda \geq 400$ nm was required to generate infrared product bands corresponding to DSiOD. Studies with a number of cutoff filters passing more energetic photons than 400 nm suggested the presence of a very broad absorption for the Si···OD$_2$ adduct. A broad, continuous absorption would be extremely difficult to see in U.V.-VIS absorption without an extremely well defined baseline.

The germanium-water adduct band has no evident band structure; rather, it displays a rather broad continuous absorption encompassing a 5,250 cm$^{-1}$ range. The broad absorption continuums noted for the silicon- and germinium-water adducts may be interpreted in the two manners
previously discussed to explain the broad absorption continuum observed for the magnesium-water adduct. First, if a molecular species is weakly bound in the ground state (but well bound in the excited state), absorption may take place from a continuous range of internuclear separations which will be reflected in a broad, continuous absorption band. Second, it is also possible to generate continuous spectra by absorption into a dissociative excited state in that the excited states of the adduct may be unbound with respect to rearrangement to form the insertion product in an excited state. The latter consideration seems reasonable in the case of the Si- and Ge-H₂O adducts, since their spectra are very high in energy (around 30,000 cm⁻¹) and have the largest red shifts from the atomic lines of all the metal systems studied. This suggests that electronic states of the HMOH species may strongly couple with the excited states of the adducts. Such possibilities will be discussed shortly in the light of molecular orbital and electronic state-to-state correlations. Although from preliminary considerations, several adduct excited states might be expected to be apparent in electronic absorption, transitions to these excited states are probably washed out by the observed broad absorption continuum.

Band intensity behavior observed during selective photolysis studies of the tin-water adduct bands suggested
that the adduct has two observable excited states. The bands, although somewhat broad, were much more discrete than the very broad Ge⋯H₂O adduct absorption band. From preliminary considerations, it was noted that the adduct should have two stable excited electronic states: 3B₁ and 3B₂ (actually two other states, 1B₁ and 1B₂, are probably stable as well but unaccessible from a triplet ground state) with the latter state being the most stable. Therefore, the low energy adduct band at 3257 Å (30,702 cm⁻¹) probably correlates with a A(3B₂) → X(3A₂) transition since the 3B₂ state is expected to be lowest in energy irrespective of large spin-orbit coupling. Unfortunately, it is not possible to unambiguously determine the nature of the state observed in absorption at 2989 Å (33,458 cm⁻¹) in that it may correspond to the 3B₁ state or, since spin-orbit coupling is consequential for the tin atom, the state may more properly correlate with one of the three spin-orbit states derived from the 3B₂ state: A₁, A₂, or B₁. The identities of the excited states corresponding to the adduct bands that grow in underneath the atomic transitions are also indeterminate since (1) the band structure is broad and obscured by being positioned underneath the atomic transitions, and (2) they may correlate with any of six spin-orbit states: A₁, A₁, A₂, B₁, B₁, and B₂.
2. ORBITAL AND STATE CORRELATIONS

The reaction dynamics of the Group IVA metal-water chemistry may be considered in the light of orbital and state correlations which may elucidate the reaction pathways that are photolytically induced. Initially, it is appropriate to examine the evolution of the molecular orbital structure of the reactants into the orbital structure of the products that allows one to evaluate the electron configurations, and hence the electronic states, of the products that are generated by chemical reaction. These state correlations derived from orbital correlations are then employed to illuminate the rigorous state-to-state correlations with the result the potential energy barriers to reaction along particular potential energy surfaces may be predicted or rationalized. A suitable molecular orbital correlation diagram for the investigation of the Group IVA metal-water interactions is depicted in Figure V-4. This MO correlation diagram analyzes the metal approaching the water molecule in two different dispositions: (1) the metal atom approaching the water molecule along the line defined by the bisection of the water's H-O-H angle so that the system remains in the $C_{2v}$ point group, and (2) the metal atom approaching the water molecule along the perpendicular bisector of the O-H bond so the system remains in the $C_3$ point group despite in-plane deviations from the bisector. This diagram depicts the formation of
FIGURE V-4

MOLECULAR ORBITAL CORRELATION DIAGRAM SUITABLE FOR THE GROUP IVA METAL–WATER INTERACTIONS
the metal-water adduct of C$_{2v}$ symmetry, and the HMOH molecule of C$_{s}$ symmetry. The molecular orbital structure of the HMOH species is expected to be quite similar to a bent HAB molecule /17/ identifying the OH fragment with the B atom. The electronic structure of the HMOH molecule is predictably similar to that of other 12 electron HAB species like HCF, HSiCl, etc. which have been studied by gas phase electronic spectroscopy. The ground state electron configuration for the 12 valence electron HMOH (M = Si, Ge, and Sn) species is expected to be

\[ \ldots (1a'')^2(6a')^2(7a')^2 \]

which corresponds to a 1A' electronic ground state with a doubly occupied highest occupied molecular orbital. HSiCl /20/ and HCF /18/ both have 1A' ground states. According to a Walsh molecular orbital correlation diagram (see Figure IV-5) for a linear and bent HAB molecule, the HMO angle should certainly be less than 180° since the 2π-7a' orbital which accounts for the bent configuration of HAB is doubly occupied. The experimental bond angles for HCF /18/ and HSIF /19/ are \( \sim 102^\circ \) and \( 100^\circ \pm 3^\circ \), respectively. A recent infrared matrix isolation study of HSIOH /5/ showed the molecule to be planar (C$_{s}$ point group) with a HSIO bond angle of \( 96.6^\circ \pm 4^\circ \). The electron configuration of the first excited state is expected to be
\[ (1a'')^2(6a')^2(7a')(2a'') \]

which corresponds to a \(^1\text{A}''\) or a \(^3\text{A}''\) excited state. The first accessible excited state of the HSiCl \(^{20}\) and HCF \(^{18}\) molecules was shown to be of \(^1\text{A}''\) symmetry. Since the predicted \(\text{A} + \text{X}\) transition (\(^1\text{A}'' + ^1\text{A}'\)) for HMOH involves promoting an electron from the \(2\pi - 7a'\) orbital to the nonbonding \(2\pi - 2a''\) orbital, the equilibrium bond angle should change dramatically in going from the ground to the excited state. Consequently, the off-axis Franck-Condon factors should be suitable to create a long progression in the bending mode that would generate a very broad band for this electronic transition. This speculation is substantiated by the reported observation of a long, densely structured absorption progression from 5,500 Å to 8,200 Å for HCCl \(^{21}\) generated by a flash photolysis of HCClBr\(_2\). This consideration, in all probability, explains why electronic absorption features were not observed for HMOH (\(M = \text{Si, Ge, and Sn}\)) during this study in that unstable baselines make detection of very broad absorptions quite difficult.

In the \(C_{2\nu}\) approach the degenerate \(p\) orbitals are split into the \(b_2\), \(b_1\), and \(a_1\) orbitals. According to the ground electronic state of the metal-water adduct, the \(b_2\) and \(b_1\) orbitals are singly occupied with electrons of unpaired spins. Since it is reasonable to believe that
the C$_{2v}$ adduct precursor must rearrange to the C$_s$ approach before the insertion reaction, it is appropriate to resolve the C$_{2v}$ symmetry species into those species for C$_s$. Accordingly, the singly occupied 3p-a' orbital of the metal correlates into the 7a' orbital of HMOH, and the singly occupied 3p-a'' orbital of the metal correlates into the 2a'' orbital of HMOH. From this orbital correlation and occupancy, a 3A'' potential energy surface is generated which correlates the ground state M(3P$_g$) + H$_2$O(1A$_1$) reactants into the . . .(6a')$^2$(7a')(2a'') configuration for the insertion product that corresponds to the 3A'' excited state of HMOH (see Figures V-5 and V-6).

Considering the silicon-water interaction (see Figure V-5), since the ground state insertion product (HSiOH) is more stable by about 59 kcal/mole (see Table V-7) relative to the reactants in their respective ground states, the 3A'' potential surface that correlates into the 3A'' excited state of the insertion product is probably still an overall exothermic process and encounters no or a very small potential energy barrier to reaction since the state correlation follows directly from the orbital correlation. The process is thought to be exothermic since the 1A'' excited state of HSiCl is only about two eV (~48 kcal/mole) above the ground state which positions the 3A'' even lower in energy. The qualitative prediction
FIGURE V-5

ELECTRONIC STATE CORRELATION DIAGRAM FOR THE SILICON–WATER INTERACTION

---- Denotes states which have not been observed.

0 Denotes an avoided surface intersection.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta H ) (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Si} + \text{H}_2\text{O} \rightarrow \text{HSiOH} )</td>
<td>(-59 \pm 10)</td>
</tr>
<tr>
<td>( \text{Si} + \text{H}_2\text{O} \rightarrow \text{SiO} + \text{H}_2 )</td>
<td>(-75 \pm 2)</td>
</tr>
<tr>
<td>( \text{HSiOH} \rightarrow \text{SiO} + \text{H}_2 )</td>
<td>(-16 \pm 10)</td>
</tr>
<tr>
<td>( \text{Ge} + \text{H}_2\text{O} \rightarrow \text{HGeOH} )</td>
<td>(-43 \pm 10)</td>
</tr>
<tr>
<td>( \text{Ge} + \text{H}_2\text{O} \rightarrow \text{GeO} + \text{H}_2 )</td>
<td>(-41 \pm 2)</td>
</tr>
<tr>
<td>( \text{HGeOH} \rightarrow \text{GeO} + \text{H}_2 )</td>
<td>(+2 \pm 10)</td>
</tr>
<tr>
<td>( \text{Sn} + \text{H}_2\text{O} \rightarrow \text{HSnOH} )</td>
<td>(-25 \pm 10)</td>
</tr>
<tr>
<td>( \text{Sn} + \text{H}_2\text{O} \rightarrow \text{SnO} + \text{H}_2 )</td>
<td>(-11 \pm 2)</td>
</tr>
<tr>
<td>( \text{HSnOH} \rightarrow \text{SnO} + \text{H}_2 )</td>
<td>(+14 \pm 10)</td>
</tr>
<tr>
<td>( \text{Pb} + \text{H}_2\text{O} \rightarrow \text{HPbOH} )</td>
<td>(+16 \pm 10)</td>
</tr>
<tr>
<td>( \text{Pb} + \text{H}_2\text{O} \rightarrow \text{PbO} + \text{H}_2 )</td>
<td>(-27 \pm 2)</td>
</tr>
<tr>
<td>( \text{HPbOH} \rightarrow \text{PbO} + \text{H}_2 )</td>
<td>(+11 \pm 10)</td>
</tr>
</tbody>
</table>

\(^a\)Heats of reaction were estimated using bond energy data from references 2, 22, and 23.
that no or a very small potential energy barrier to reaction exists along the $3^A''$ potential surface is corroborated by the fact that the infrared studies observed spontaneous rearrangement of the Si···OH$_2$ adduct in an argon matrix at 15 K to form HSiOH via hydrogen tunneling. The orbital occupancy that would be required to generate a $^1A'$ surface that would correlate adiabatically into the $^1A'$ ground state of HSiOH corresponds to a doubly occupied $b_1$ orbital of the precursor adduct ($^1A_1$). So the $^1D_g + ^1A_1$ reactant combination correlates into the $^1A'$ ground state of the insertion species. This combination also correlates into the $^1A'$ excited state of HMOH although through a different adduct orbital occupancy.

Figure V-6 shows the state-to-state correlation diagram for the germanium-water chemical interaction which is fundamentally identical to that of the silicon-water interaction diagram except for quantitative detail. The Ge···OH$_2$ adduct in its $^3B_2$ ground state derived from the $^3P_g + ^1A_1$ combination correlates adiabatically into the $^3A''$ excited state of HGeOH without encountering any surface intersections. Table V-7 indicates that the reaction of Ge into the OH bond of water is exothermic by about 43 kcal/mole, one-third lower than that noted for the silicon insertion. Although the $^3A''$ excited state of HGeOH has not been observed spectroscopically,
FIGURE V-6

ELECTRONIC STATE CORRELATION DIAGRAM FOR THE GERMANIUM-WATER INTERACTION

---- Denotes states which have not been observed.

0 Denotes an avoided surface intersection.
the energy of transition may be roughly estimated by assuming the value is close to the $^1A'' + ^1A'$ transition of HSiCl as was done in the Si-H$_2$O correlation diagram. This argument leads to the conclusion that the $^3A''$ of the HGeOH is higher in energy relative to the $^3A''$ reactant state derived from $^3P_g + ^1A_1$. Consequently, the insertion reaction of germanium, although suitably exothermic, is not expected to occur for two reasons: (1) the HMOH $^1A'$ ground state correlates to an excited $^1A'$ state of the reactants derived from the $^1D_g + ^1A_1$ combination and (2) reaction along the ground $^3A''$ surface of the reactants derived from the $^3P_g + ^1A_1$ combination is hindered by a potential energy barrier generated by the endothermicity of the reaction to form HGeOH in its $^3A''$ excited state which was not encountered in the Si-H$_2$O reaction because this process is more exothermic. This analysis rationalizes the different chemical behavior observed for these two chemical systems in the infrared studies which reported spontaneous Si···OH$_2$ rearrangement to form HS1OH via tunneling, whereas Ge···OH$_2$ was reported to be stable with regard to spontaneous rearrangement and required photolysis to generate HGeOH.

It is of interest to try to understand the nature of the photochemical channel that is pursued by the reactant when the insertion reactions are induced by photolysis. In view of the very broad character of the adduct absorptions for the silicon and germanium adducts, it was
speculated that these states may strongly couple into excited states of the insertion product and hence be unstable with respect to rearrangement. Figures V-5 and V-6 show that this is possible. The ground state for the adduct in the C₂ᵥ point group is ³A₂. The first excited state of the adduct is believed to be ³B₂ derived from the ³Pᵤ + ¹A₁ combination. This state resolves into ³A' in the Cₛ point group. Diabatically, this ³A' surface correlates into a highly excited ³A' state of HMOH; however, there is an avoided surface crossing with a ³A' charge-transfer surface derived from M⁺(²Pᵤ) + H₂O⁻(²A₁) which correlates diabatically to a lower ³A' state. Therefore, adiabatically the ³A' (³Pᵤ + ¹A₁) surface exothermically correlates into the lower ³A' state of HMOH which can then relax to the ground state. Since the ionization potential of M(³Pᵤ) is only about 3.1 eV, and the electron affinity of water (¹A₁) is about zero, the surface intersection may be expected to occur early in the stages of rearrangement of the complex to form HMOH so not only may a potential energy barrier fail to develop, but the ³A' state may be unbound with respect to the insertion reaction. Nevertheless, even though these considerations rationalize the nature of the observed broad absorption for the adduct, rearrangement would certainly be possible for the Si···OD₂ adduct along the ground state ³A" surface, since it is partially activated after electronic relaxation.
The tin-water system is not treated according to molecular orbital and state correlations since the important role that spin-orbit coupling plays in this species severely complicates the issue to the point reaction pathways become quite ambiguous.
REFERENCES


CHAPTER SIX

ELECTRONIC ABSorption AND EMISSION STUDIES OF
THE GROUP IIa METAL SUBOXIDES ISOLATED IN
CRYOGENIC RARE GAS MATRICES
CHAPTER SIX

OUTLINE

VI. ELECTRONIC ABSORPTION AND EMISSION STUDIES OF THE GROUP IIIA METAL SUBOXIDES ISOLATED IN CRYOGENIC RARE GAS MATRICES

A. INTRODUCTION

B. EXPERIMENTAL

C. RESULTS AND DISCUSSION
   1. ALUMINUM SUBOXIDE
   2. GALLIUM SUBOXIDE
   3. INDIUM SUBOXIDE

D. CONCLUSION
VI. ELECTRONIC ABSORPTION AND EMISSION STUDIES OF THE GROUP IIIA METAL SUBOXIDES ISOLATED IN CRYOGENIC RARE GAS MATRICES

A. INTRODUCTION

Over the past two decades the Group IIIA metal suboxides, Al$_2$O, Ga$_2$O, In$_2$O, and Tl$_2$O, have been studied by a variety of techniques /1-18/; however, conclusions regarding their equilibrium geometries and molecular properties have had quite a controversial history. It was noted that the structure of Al$_2$O potentially could conform according to the symmetry elements of four different point groups: C$_s$, C$_{av}$, (asymmetrical conformations: Al-Al-O) C$_{2v}$, or D$_{oh}$ (symmetrical conformations: Al-O-Al). However, thermo-dynamic arguments based on M-O and M-M bond dissociation energies were later shown to rule out the C$_s$ or C$_{av}$ asymmetrical conformations /3/. Prior to experimental evidence, Al$_2$O was believed to have a bent C$_{2v}$ symmetrical structure /1/. Results of electric deflection studies /2/, however, suggested that Al$_2$O has a linear D$_{oh}$ structure, since it was observed that a molecular beam of Al$_2$O was not refocused by an inhomogeneous quadrupole electric field which indicates the molecular dipole moment of Al$_2$O is small. Büchler, et al. /2/ pointed out that this
result does not have strong geometric implications since they considered it likely that the AlO bond moment in Al₂O is also small; however, in view of the electropositive character of Al, they proposed that Al₂O is linear.

In 1964, gas phase infrared absorption measurements /4/ indicated that the Al₂O molecule is linear, whereas Ga₂O and In₂O are bent. This result was in contrast to matrix isolation studies /3/ conducted that very same year whose results indicated that Al₂O is bent with an apex angle near 145° and has a ν₂ bending mode frequency below 250 cm⁻¹. The prediction of this low value for the bending mode frequency was instrumental in altering the conclusions drawn from electron diffraction studies on Ga₂O and In₂O which initially reported in 1965 /5/ that these species have bent symmetrical structures with apex angles between 130° and 160°. In 1968 /6/, to take into account large vibrational distortions arising from ν₂ frequencies estimated to exist below 200 cm⁻¹, the electron diffraction data were reassessed to lead to a revised conclusion stating that Ga₂O and In₂O are linear. Hinchcliffe and Ogden /7/ in 1969 reported precise infrared measurements of the ν₃ fundamentals of matrix isolated Ga₂O, In₂O, and Tl₂O and their respective oxygen-18 isomers. Using the oxygen isotopic shift values, they calculated apex angles of 143°, 135°, and 131° for Ga₂O, In₂O, and
$\text{Tl}_2\text{O}$, respectively, on the basis of a $C_{2v}$ structure. These results concur with the original conclusions of the electron diffractions studies. Additionally in 1969, Shevel'kov et. al. /18/ detected both the symmetric, $v_1(A_1)$, and asymmetric $v_3(B_1)$, modes of $\text{Tl}_2\text{O}$ which bolsters the credibility of a bent conformation for $\text{Tl}_2\text{O}$. These authors made an assignment for a combination band which placed the bending mode frequency for $\text{Tl}_2\text{O}$ in the region of 130 cm$^{-1}$.

In 1970, Snelson /9/ reported the observation of the symmetric and asymmetric stretching modes of $\text{Al}_2\text{O}$ but was unable to observe the bending mode frequency, $v_2$, down to 190 cm$^{-1}$. By analogy with $\text{Li}_2\text{O}$, he predicted the $v_2$ band of $\text{Al}_2\text{O}$ to occur near 120 cm$^{-1}$ which by mass considerations alone, positions the heavier suboxides below 100 cm$^{-1}$. In the same year, Makowiecki et. al. /11/ reported assignments for the three fundamental vibrational modes of the aluminum family suboxide molecules isolated in rare gas matrices. The results of this study showed that the $v_2$ mode lies more than 200 cm$^{-1}$ above the energies expected on the basis of previous reasonable estimates. They suggested that this result may be evidence in support of metal-metal bonding being involved in the structures of these molecules. In 1971, Brom et al. /10/ reported quite different frequencies for the $v_1$ and $v_2$ modes of $\text{Tl}_2\text{O}$. From isotope shift data, these investigators concluded that $\text{Tl}_2\text{O}$ has
a 90° apex angle which they interpreted in terms of a strong Ti-Ti bond which is in agreement with the results of high temperature mass spectrometric studies of Ti₂O₃ by Cubicciotti /21/. Hinchcliffe and Ogden /12/ have made infrared measurements of the matrix isolated Ga₂O, In₂O, and Ti₂O molecules with ⁰¹⁸- enriched samples. An analysis of the isotopic splittings and diffusion behavior demonstrated that the bands attributed to the ν₁ and ν₂ fundamentals of Ga₂O, In₂O, and possibly Ti₂O in previous studies /3,10,11/ have been incorrectly assigned and more appropriately correlate with a mode of some aggregate species, perhaps the dimer of M₂O. Performing the same type of experiments with ⁰¹⁸- enriched Al₂O, Marino and White /14/ and Carlson et al. /15/ have reassigned the ν₁ and ν₂ fundamentals to a high aggregate of Al₂O as well. Marino and White /14/ reported that there is no evidence for even a very weak feature in the 500 cm⁻¹ vicinity where ν₂ was previously reported to absorb until molecular oxygen is introduced into the argon stream. Giving meticulous attention to concentration and diffusion behavior, Hinchcliffe and Ogden /13/ have reinvestigated the infrared absorptions of Ga₂O and In₂O isolated in nitrogen matrices. They make infrared measurements for the ν₁ and the ν₃ symmetric and asymmetric stretching frequencies of Ga₂O at 809 cm⁻¹ and 472 cm⁻¹ and of In₂O at 722 cm⁻¹ and 442 cm⁻¹, respectively. Since the ν₁
bands were quite weak so as to preclude isotopic substitution studies, these authors point out that their assignments are tentative. From isotopic shift data on \( v_3 \) derived from \( O^{18} \)-enriched studies, the authors calculated apex angles of \( \geq 142^\circ \) and \( \geq 135^\circ \) for \( Ga_2O \) and \( In_2O \), respectively. However, they discuss that the inclusion of a modest anharmonic correction results in an apex angle much closer to \( 180^\circ \) for \( Ga_2O \) and \( In_2O \), but the observation of the symmetric stretching mode \( (A_1) \) substantiates a bent configuration. Wagner /16/ has performed \( ab \) \( initio \) calculations on \( Al_2O \) whose results predict a linear symmetrical structure for \( Al_2O \) with \( v_1, v_2, \) and \( v_3 \) vibrational frequencies of 1057 cm\(^{-1}\), 527 cm\(^{-1}\), and 102 cm\(^{-1}\), respectively. Consequently, as a result of a large number of investigations of the Group IIIIA metal suboxides which span over a period of about 15 years, the asymmetrical stretching frequencies for \( Al_2O, Ga_2O, In_2O, \) and \( Tl_2O \) have been unequivocally established; however, the bending mode frequencies for these four molecules are still unknown experimentally. Tentative assignments for the symmetric stretching modes of \( Ga_2O \) and \( In_2O \) have been made and experimental evidence indicates that they are bent; however, the symmetric stretching mode and the equilibrium conformation of \( Al_2O \) are still not established by experimental evidence.
There have been several electronic absorption studies of $\text{Al}_2\text{O}$. Linevsky et al. /3/ assigned bands observed in the U.V. portion of the spectrum to an electronic transition of $\text{Al}_2\text{O}$ since there were satisfactory vibrational progressions; however, McDonald and Innes /22/ later showed that these bands are attributable to the $^2\Delta_1 + A^2\Pi_1$ system of $\text{AlO}$. Finn et al. /18/ tentatively assigned a previously unreported band located around 25,000 cm$^{-1}$ to an electronic transition of $\text{Al}_2\text{O}$ isolated in a krypton matrix. Using a Dupont curve resolver, the band was deconvoluted into four Gaussian components whose maxima lie at 24,380 cm$^{-1}$, 24,590 cm$^{-1}$, 24,800 cm$^{-1}$, and 25,010 cm$^{-1}$ with normalized absorbances of 0.16, 0.26, 0.40, and 0.18, and an average vibrational separation of 210 cm$^{-1}$.

The purpose of this study is to investigate the electronic structures of the $\text{Al}_2\text{O}$, $\text{Ga}_2\text{O}$, and $\text{In}_2\text{O}$ molecules utilizing U.V.-VIS absorption and emission spectroscopy to document new excited states for these species as well as to obtain new values for the $\nu_1$ and $\nu_2$ vibrational modes in the ground and excited states of these metal suboxides.

B. EXPERIMENTAL

The furnace assembly, the matrix isolation apparatus, and the absorption and emission spectrometer have been
previously described in chapter two of this dissertation; however, more explicit details regarding the LIF operation are pertinent at this juncture. The laser utilized to induce fluorescence in this work was a Chromatix CMX-4 tunable flashlamp pumped dye laser with a one microsecond pulsewidth. Second-harmonic ADP doubling crystals were employed to access the 265 to 310 nm U.V. region which was necessary to excite the U.V. transitions of the metal suboxides. The wavelengths of laser excitation were 2662 Å, 2660 Å, and 3059 Å for Al₃O, Ga₂O, and In₂O, respectively. Rhodamine 6G and Coumarin 504 dyes were used to generate the fundamentals required for second-harmonic generation (SHG). A Corning CS 7-54 filter was interposed to isolate the fundamental frequency from the SHG of the fundamental.

The output of the photomultiplier tube was amplified with a PAR Model 113 preamplifier and then preintegrated (RC = 10 µs) before signal recovery with a boxcar integrator constructed from Evans Associates modules. The boxcar had a one microsecond aperture for signal sampling which was delayed six microseconds ± 100 ns from the laser pump pulse. All of the reported spectra are uncorrected for the photomultiplier tube's response.

Vapors of the metal suboxides were produced by the reaction of the pure liquid metal reducing the solid metal sesquioxide at elevated temperatures, i.e.,
\[ 4M(1) + M_2O_3(s) \rightarrow M_2O(g) \]

It has been fairly well established from mass spectrometric studies /19,20/ that the predominate vapor species above such samples is the metal suboxide with less than 10% metal atoms and no other significant species. Aluminum and gallium metals were procured at 99.9% purity. The indium metal was obtained from a laboratory source at an unknown purity. The metal sesquioxides had a stated purity \( \geq 99.9\% \). All of the metal suboxides were vaporized from cylindrical alumina crucibles. The furnace-cell assembly was outgassed for two hours prior to deposition at temperatures in excess of those required for deposition. System pressure after outgassing was less than \( 1 \times 10^{-7} \) mm Hg. Host-to-guest ratios in the matrices were measured with the quartz crystal microbalance and will be reported for each experiment. Research grade purity (99.995%) argon and krypton were employed as host mediums. Each matrix sample required 15 minutes to prepare.

C. RESULTS AND DISCUSSION

1. ALUMINUM SUBOXIDE

Three categories of experiments were conducted: (1) electronic absorption studies of \( \text{Al}_2\text{O} \) isolated in krypton, (2) electronic absorption studies of \( \text{Al}_2\text{O} \) isolated in argon, and (3) laser induced emission studies of \( \text{Al}_2\text{O} \).
isolated in krypton. Each category of experiment was repeated several times to insure replicability, to vary concentration parameters, and to test for diffusion behavior. Figure VI-1 depicts the U.V.-VIS absorption spectrum of Al₂O isolated in a krypton matrix at 15 K. Table VI-1 lists the assignments corresponding to the band maxima. In absorption two electronic systems, A + X and C + X, were observed for Al₂O. Annealing the matrix had no effect on the band structure except for a slight sharpening of the bands. Annealing did effect an enhancement of the intensity of several weak bands in the deep U.V. which are presumable attributable to aggregate species since they are only apparent in matrices prepared with heavier depositions of Al₂O. The most prominent system is the C + X transition which has its 000-000 band at 2744 Å (36,144 cm⁻¹) corresponding to the peak labeled 000. This band origin assignment is bolstered by the results of emission studies of Al₂O. This system displays progressions in two vibrational modes in the excited state. The average separations of successive bands in one progression is 186 cm⁻¹ while the other sequence of bands is separated by about 454 cm⁻¹. Table VI-9 lists the average vibrational spacings for different electronic states of the Group IIIA metal suboxides isolated in argon and krypton matrices. The most reliable estimates for ν₂ in the ground state predict frequencies below 200 cm⁻¹, and the ν₃ frequency
FIGURE VI-1

ELECTRONIC ABSORPTION SPECTRUM FOR ALUMINUM SUBOXIDE ISOLATED IN A KRYPTON MATRIX

$\text{Al}_2\text{O}:\text{Kr} = 1:660$

$T \approx 1160^\circ \text{C}$
### TABLE VI-1

**Assignments for the Optical Absorption Spectra of Aluminum Suboxide Isolated in a Krypton Matrix**

<table>
<thead>
<tr>
<th>Peak</th>
<th>$\lambda(\AA)$</th>
<th>$\tilde{\nu}^a$</th>
<th>Assignment$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A+X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>000</td>
<td>4294</td>
<td>23 286</td>
<td>A(000) + X$^d$(000)$^c$</td>
</tr>
<tr>
<td>010</td>
<td>4272</td>
<td>23 408</td>
<td>A(010) + X(000)</td>
</tr>
<tr>
<td>100</td>
<td>4207</td>
<td>23 768</td>
<td>A(100) + X(000)</td>
</tr>
<tr>
<td>110</td>
<td>4183</td>
<td>23 907</td>
<td>A(110) + X(000)</td>
</tr>
<tr>
<td>120</td>
<td>4159</td>
<td>24 045</td>
<td>A(120) + X(000)</td>
</tr>
<tr>
<td>C+X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>000</td>
<td>2744</td>
<td>36 444</td>
<td>C(000) + X(000)</td>
</tr>
<tr>
<td>010</td>
<td>2731</td>
<td>36 621</td>
<td>C(010) + X(000)</td>
</tr>
<tr>
<td>100</td>
<td>2711</td>
<td>36 891</td>
<td>C(100) + X(000)</td>
</tr>
<tr>
<td>110</td>
<td>2696</td>
<td>37 085</td>
<td>C(110) + X(000)</td>
</tr>
<tr>
<td>200</td>
<td>2677</td>
<td>37 352</td>
<td>C(200) + X(000)</td>
</tr>
</tbody>
</table>

$^a$ ± 15 cm$^{-1}$.

$^b$ Band energies are taken from band maxima.

$^c$ ($v_1$, $v_2$, $v_3$).

$^d$ Probably $^1\Sigma^+$ for the linear case or $^1A_1$ if slightly bent.
in the ground state of Al₂O has been measured to be nearly 1000 cm⁻¹. Consequently, it is reasonable to assume that the progression with a 186 cm⁻¹ average spacing is in the bending mode while the 454 cm⁻¹ progression is in the symmetrical stretching mode. It is only remotely possible that the ν₂ or ν₃ frequencies would decrease by a factor of two in the excited state relative to the ground state frequencies. The A + X band system has its 000-000 band at 2744 Å (36,444 cm⁻¹) corresponding to the peak labeled 000. The band structure was washed out in the emission study of Al₂O which precludes substantiation of the band origin. As was noted for the C + X band system, this system displays short progressions in two vibrational modes. One progression has an average spacing of 133 cm⁻¹, while the other progression has an average separation of 482 cm⁻¹; consequently, in analogy with the C + X system, the two progressions are assigned to the ν₂ and the ν₁ vibrational modes, respectively.

Figure VI-2 depicts the electronic absorption spectrum of Al₂O isolated in an excess of argon at 15 K. Table VI-2 lists the assignments corresponding to band maxima. In this experiment, only the C + X transition was studied which displayed progressions in the ν₁ and ν₂ modes with average spacings of 451 cm⁻¹ and 156 cm⁻¹, respectively. The C + X band system is more discrete in
FIGURE VI-2

ELECTRONIC ABSORPTION SPECTRUM FOR
ALUMINUM SUBOXIDE ISOLATED IN AN ARGON MATRIX

Al₂O:Ar = 1:6415
TABLE VI-2
ASSIGNMENTS FOR THE OPTICAL ABSORPTION SPECTRA
OF ALUMINUM SUBOXIDE ISOLATED IN AN ARGON MATRIX

<table>
<thead>
<tr>
<th>Peak</th>
<th>$\lambda(\overset{\not{\circ}}{\AA})$</th>
<th>$\nu$(cm$^{-1}$)$^a$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>000</td>
<td>2694</td>
<td>37 121</td>
<td>$C(000) + X^d(000)^c$</td>
</tr>
<tr>
<td>010</td>
<td>2682</td>
<td>37 284</td>
<td>$C(010) + X(000)$</td>
</tr>
<tr>
<td>100</td>
<td>2663</td>
<td>37 558</td>
<td>$C(100) + X(000)$</td>
</tr>
<tr>
<td>110</td>
<td>2652</td>
<td>37 707</td>
<td>$C(110) + X(000)$</td>
</tr>
<tr>
<td>200</td>
<td>2630</td>
<td>38 024</td>
<td>$C(200) + X(000)$</td>
</tr>
</tbody>
</table>

$^a$ ± 15 cm$^{-1}$.

$^b$ Band energies are taken from band maxima.

$^c$ $(\nu_1, \nu_2, \nu_3)$.

$^d$ Probably $E_g^+$ for the linear conformation or $A_1$ if slightly bent.
argon compared to krypton in that the band progressions were not observed as blue or red shoulders on more intense bands as often as was observed in krypton. Table VI-10 lists the energies of the excited states of the metal suboxides isolated in argon and krypton matrices. The band origin is blue shifted by 677 cm\(^{-1}\) in argon relative to krypton which is predictable since argon has a lower polarizability compared to krypton. The symmetric stretching frequency decreases by only three wavenumbers as a consequence of switching to an argon host, but the bending mode frequency decreases by 30 cm\(^{-1}\). Unfortunately, the error bars on these values are so large that they forestall any meaningful discussion of these shifts.

Figure VI-3 shows the laser induced emission spectrum of Al\(_2\)O isolated in krypton with an excitation wavelength of 2662 Å. Table VI-3 lists the assignments for the band maxima. Emission was observed from three excited states of Al\(_2\)O. The reported spectrum only displays the B \(\rightarrow\) X and C \(\rightarrow\) X band systems since the A \(\rightarrow\) X emission system has no resolvable bands and is very broad and weak. The C \(\rightarrow\) X emission system has its 000-000 band at 2760 Å (36,233 cm\(^{-1}\)) corresponding to the intense band labeled 000. This 000-000 band is red shifted by 211 cm\(^{-1}\) relative to the 000-000 band observed in absorption. A red shift in the band origin is expected in emission since an endoergic
FIGURE VI-3
LASER INDUCED EMISSION SPECTRUM FOR
ALUMINUM SUBOXIDE ISOLATED IN A KRYPTON MATRIX

$\text{Al}_2\text{O:Kr} = 1:2525$

Laser Excitation $\lambda = 2662 \text{ Å}$


<table>
<thead>
<tr>
<th>Peak</th>
<th>λ (Å)</th>
<th>$\bar{\nu}$ (cm$^{-1}$)$^a$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A^d,f$</td>
<td>5294</td>
<td>18 890</td>
<td>$A \rightarrow X^d$</td>
</tr>
<tr>
<td>$A^f$</td>
<td>4066</td>
<td>24 595</td>
<td>$A \rightarrow X$</td>
</tr>
<tr>
<td>$A^{e,f}$</td>
<td>3660</td>
<td>27 322</td>
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<tr>
<td>000</td>
<td>2913</td>
<td>34 331</td>
<td>$B(000) \rightarrow X(000)^c$</td>
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<td>35 292</td>
<td>$C(000) \rightarrow X(200)$</td>
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<td>35 772</td>
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</tr>
<tr>
<td>000</td>
<td>2760</td>
<td>36 233</td>
<td>$C(000) \rightarrow X(000)$</td>
</tr>
</tbody>
</table>

$^a$ ± 15 cm$^{-1}$.

$^b$ Band energies are taken from band maxima unless noted otherwise.

$^c$ ($\nu_1, \nu_2, \nu_3$).

$^d$ Red onset.

$^e$ Blue cutoff.

$^f$ Not shown in spectra.

$^g$ Probably $^{1}2_{g}$ for the linear conformation or $^{1}A_{1}$ if slightly bent.
solvent cage reorganization is often required in absorption to an excited state but not in relaxation to the ground state. Because of the near coincidence of the 000-000 bands observed in absorption and in emission, the vibrational band numbering of the C-\(X\) band system is believed to be accurate. This emission system displays a progression in a single vibrational mode in the ground state. The average separation of successive bands is 471 cm\(^{-1}\) ± 15 cm\(^{-1}\). Since the \(v_3\) frequency of Al\(_2\)O in the ground state has been measured to be 991.7 cm\(^{-1}\) in an argon matrix /11/, and the \(v_2\) frequency is predictably below 200 cm\(^{-1}\), by elimination the progression is assigned to be in the symmetrical stretching mode, \(v_\perp\). This value for \(v_\perp\) of Al\(_2\)O compares favorably with the most recent \(v_\perp\) values for Ga\(_2\)O and In\(_2\)O /13/ which are reported to be 472 cm\(^{-1}\) and 442 cm\(^{-1}\), respectively. This \(v_\perp\) value for Al\(_2\)O is also near the 527 cm\(^{-1}\) \(v_\perp\) value calculated by SCF techniques /16/ whose results are normally higher in energy relative to the actual value. The weak band labeled 000 is assigned to a \(B \rightarrow X\) transition. As will be discussed shortly, the analogous \(B \rightarrow X\) emission systems for the Ga\(_2\)O and In\(_2\)O molecules are increasingly more intense. In fact, the \(B \rightarrow X\) system was observed in absorption for In\(_2\)O. This behavior suggests that the \(B\) excited state may actually correspond to a triplet state with the same orbital occupation as the \(C\) state since for the heavier metals, spin-
orbit coupling becomes increasingly significant, and the ground state probably has singlet multiplicity /16/. It is interesting that the A - X system displays fairly discrete band structure in absorption but is very broad and continuous in emission. This may suggest that there is a sufficient difference in the equilibrium conformations of the ground and excited states so as to favor the Franck-Condon factors in emission to portions of the ground state potential energy surface that are repulsive in nature. Absorption and emission spectra of highly dilute concentrations of Al₂O in Kr matrices were identical to those presented in this paper which eliminates the possibility of confusion of these previously discussed bands with those bands attributable to aggregate species.

Wagner /16/ has calculated the ground state configuration of Al₂O to be 

\[ (1\sigma_u)^2(1\sigma_g)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^4(3\sigma_u)^2 \]

\[ (4\sigma_g)^2(5\sigma_g)^2(4\sigma_y)^2(2\pi_u)^4(6\sigma_g)^2(5\sigma_u)^2 \]

which corresponds to a \( ^1\Sigma^+ \) ground state for the linear conformation or \( ^1A_1 \) for a \( C_{2v} \) structure. A population analysis of Al₂O supports a strongly ionic structure which, in turn, supports the plausibility of a linear structure for this molecule.
According to the selection rules and the Franck-Condon principle, a progression in the symmetric stretching mode is fully allowed for a linear-linear, bent-linear, or bent-bent transition assuming that there is negligible vibronic (Renner-Teller) interaction. A progression in the bending mode is fully allowed for a bent-bent or bent-linear transition; however, a progression in the bending mode is not probable for a linear-linear transition and only even changes are allowed by the selection rules. Since a progression in $v_2$ was observed in absorption from the ground state of $\text{Al}_2\text{O}$, this implies that at least either the ground or the excited state is bent, and perhaps both are bent.

An analysis of the emission results strongly suggests that the ground state of $\text{Al}_2\text{O}$ is of $D_{\infty h}$ symmetry. The normal coordinates of linear $\text{Al}_2\text{O}$ have irreducible representations given by $\Gamma_{\text{vib}} = \Sigma_g^+ + \Sigma_u^+ + \Pi_u$. The symmetric stretching mode, $\Sigma_g^+$, is infrared inactive. However, nonlinear $C_{2v}$ $\text{Al}_2\text{O}$ has normal mode symmetries given by $\Gamma_{\text{vib}} = 2A_1 + B_2$ which are all infrared active. This study has established the previously unobserved frequency for the $v_1$ mode of $\text{Al}_2\text{O}$ as being 471 cm$^{-1}$. Coupling this result with the fact that meticulous scrutiny of the 500 cm$^{-1}$ region by Marino and White /14/, who were looking for a band assignable to the bending mode frequency, failed to yield "evidence for even a very weak feature" suggests that the $v_1(\Sigma_g^+)$ mode is infrared inactive in accord with a linear $D_{\infty h}$ structure. Although these results can not unambiguously establish a linear structure for
Al₂O, they do suggest a bond angle very close to 180° in contrast to the previously reported value of 140° /3/. In the same regard, since the ν₁ modes for Ga₂O and In₂O were observed /13/, their equilibrium conformations in the ground state are by implication bent. This result also implies that the A and C excited states of Al₂O are bent.

As discussed in the introduction of this chapter, electron deflection studies /2/ suggested that Al₂O is linear, and ab initio calculations by Wagner /16/ predicted a linear ground state equilibrium conformation for Al₂O. Wagner points out that the inclusion of d orbitals in his treatment would be inconsequential since the d orbital energies on the relevant atoms and ions are too high to have significant contributions. He also discounts the possibility of a "Renner Effect" operating in this molecule on the grounds that such large Renner distortions that would be required to rationalize a bent Al₂O are not expected.

To further bolster the assignment of a linear structure to Al₂O, it is of interest to invoke the metal-metal bonding arguments employed by Makowiecki et al. /11/ which they used to rationalize the high ν₂ values (now recognized as being misassigned) of the Group IIIA metal suboxides. First, the atomization energies of all but Al₂O are in best agreement with bond energy calculations
establish a linear structure for Al$_2$O, they do suggest a bond angle very close to 180$^\circ$ in contrast to the previously reported value of 140$^\circ$ /3/. In the same regard, since the $\nu_1$ modes for Ga$_2$O and In$_2$O were observed /13/, their equilibrium conformations in the ground state are by implication bent. This result also implies that the A and C excited states of Al$_2$O are bent.

As discussed in the introduction of this chapter, electron deflection studies /2/ suggested that Al$_2$O is linear, and *ab initio* calculations by Wagner /15/ predicted a linear ground state equilibrium conformation for Al$_2$O. Wagner points out that the inclusion of d orbitals in his treatment would be inconsequential since the d orbital energies on the relevant atoms and ions are too high to have significant contributions. He also discounts the possibility of a "Renner Effect" operating in this molecule on the grounds that such large Renner distortions that would be required to rationalize a bent Al$_2$O are not expected.

To further bolster the assignment of a linear structure to Al$_2$O, it is of interest to invoke the metal-metal bonding arguments employed by Makowiecki et al. /11/ which they used to rationalize the high $\nu_2$ values (now recognized as being misassigned) of the Group IIIA metal suboxides. First, the atomization energies of all but Al$_2$O are in best agreement with bond energy calculations
involving a metal-metal bond dissociation in addition to two metal-oxygen bond dissociations. Second, electron impact fragmentation studies of the $M_2O$ species give relatively considerable concentrations of $M^+_2$ except for $Al_2O$. Cubiciotti /21/ pointed out the geometrical implications this result may have for $Tl_2O$. These arguments for the existence of metal-metal bonding in most of the metal suboxides also support the contention that $Al_2O$ is linear, and that $Ga_2O$ and $In_2O$ are bent (and hence may have limited metal-metal bonding) which was previously suggested on the basis of the visibility of the $v_1$ mode in the infrared spectra of matrix isolated $M_2O$.

The only experimental evidence that conflicts with a linear assignment for the equilibrium structure of $Al_2O$ is that derived from an analysis of isotopic shift data for the asymmetric stretching frequencies of $O^{18}$ and $O^{16}$ $Al_2O$ /3/. However, such an isotopic analysis can be plagued by serious error since the apex angle is calculated from an equation which has rigorous application for only completely harmonic motion. Specifically, if one assumes that the vibrations of a $C_{2v}$ $XY_2$ molecule are totally harmonic, the zero-order asymmetric stretching frequency is given by

$$4\pi^2\omega_3^2 = (F_r - F_{rr})(\mu_y + 2\mu_x\sin^2\theta)$$  (1)
where $\mu$ is the reduced mass and $2\theta$ is the YXY apex angle. $F_r$ and $F_{rr}$ are the principal and interaction stretching constants, respectively. If one knows $\omega_3$ for two isotopic molecules, $\text{Al}_2\text{O}^{16}$ and $\text{Al}_2\text{O}^{18}$, this equation indicates that one may calculate the apex angle according to

$$\frac{\omega_3(0^{16})}{\omega_3(0^{18})} = \left[ \frac{\mu(\text{Al}) + 2\mu(0^{16})(\sin^2\theta)}{\mu(\text{Al}) + 2\mu(0^{18})(\sin^2\theta)} \right]^{1/4} \quad (2)$$

Unfortunately, however, experiments yield absorption frequencies that are uncorrected for anharmonicity. It has been shown that if the observed $\nu_3$ frequency ratio is used to calculate $\theta$ via equation (2), the values obtained for $\theta$ represent a lower limit to the true value /23/. Linevsky et al. /3/ report infrared measurements for the $0^{16}$ and $0^{18}$ isomers of $\text{Al}_2\text{O}$ as being $994 \text{ cm}^{-1} \pm 0.5 \text{ cm}^{-1}$ and $951 \text{ cm}^{-1} \pm 0.5 \text{ cm}^{-1}$, respectively, from which they calculate an isotope ratio of $1.045 \pm 0.001$. Using equation (2) one calculates a bond angle of $150^\circ$ with attendant error limits of $+30^\circ$ and $-15^\circ$ from the error limits on the isotope ratio alone. Considering the role anharmonicity plays in the bond angle calculation, if one assumes that the observed $\text{Al}_2\text{O} \nu_3$ frequency is related to the corresponding zero-order frequency by

$$\nu_3 = \omega_3(1 - \alpha) \quad (3)$$

and estimating the anharmonicity correction ($\omega_3^{16} \alpha^{16}$) to
be 10.0 cm\(^{-1}\), then \(\omega_3\) of \(\text{Al}_2\text{O}^{16}\) is positioned at 1004 cm\(^{-1}\). Assuming the Darling-Dennision rule /24/, the corresponding zero-order frequency for \(\text{Al}_2\text{O}^{18}\) lies at 960 cm\(^{-1}\). The bond angle one calculates from this isotopic ratio is very near 180°. Diatomic AlO, which absorbs at 965.3 cm\(^{-1}\), has a zero-order frequency of 979.2 cm\(^{-1}\), so the estimated 10 cm\(^{-1}\) anharmonicity correction assumed here is not unreasonable. Therefore, considering the error limits in the infrared measurements of the isotopic \(\nu_3\) frequencies and the role anharmonicity may play to invalidate the observed frequencies with regard to their employment in equation (2), the result of the isotopic shift data which indicates \(\text{Al}_2\text{O}\) is bent is very questionable indeed.

The A + X band system observed for \(\text{Al}_2\text{O}\) isolated in krypton at 15 K in this study differs significantly with the electronic band system for \(\text{Al}_2\text{O}\) in krypton at 15 K observed by Finn et al. /18/. This study reports a band origin at 23,286 cm\(^{-1}\) with two progressions in \(\nu_1(482\ \text{cm}^{-1})\) and \(\nu_2(133\ \text{cm}^{-1})\) for the A - X system, whereas Finn and coworkers report the first red band to be at 24,380 cm\(^{-1}\) with a single progression having an average separation of 210 cm\(^{-1}\). Since identical host media were employed at the same temperature, it is difficult to reconcile the differences in the band systems observed in these two studies. However, it seems reasonable that Finn and coworkers may be misassigning
this band system since careful concentration studies of aluminum in a krypton matrix (chapter four of this dissertation) were successful in establishing that the aluminum dimer has a B - X system in this very same region of the spectrum showing an average vibrational separation of 245 cm\(^{-1}\) with the first band positioned at 23,493 cm\(^{-1}\). Since the Finn band system correlates significantly better with the B - X system of Al\(_2\), it is reasonable to assume that their assignment of this system to Al\(_2\)O is not correct.

2. **GALLIUM SUBOXIDE**

Figure VI-4 depicts the U.V.-VIS absorption spectrum of Ga\(_2\)O isolated in a krypton matrix at 15 K. Table VI-4 lists the assignments corresponding to band maxima. In absorption, only one band system is apparent which is assigned to the C - X transition for Ga\(_2\)O. Annealing the matrix had no effect other than to slightly sharpen the band structure. The 000-000 band for this system is assigned to the band labeled 000 at 2757 Å (36,226 cm\(^{-1}\)); however, the band numbering is tentative since no emission was observed from this state in the LIF study of Ga\(_2\)O. The band labeled 010 is separated by 218 cm\(^{-1}\) from the 000 band and hence for similar reasons as those described for Al\(_2\)O, is assigned to a single progression in the bending mode. Upon first consideration, this frequency
FIGURE VI-4
ELECTRONIC ABSORPTION SPECTRUM FOR
GALLIUM SUBOXIDE ISOLATED IN A KRYPTON MATRIX

$\text{Ga}_2\text{O:Kr} = 1:4450$
TABLE VI-4
ASSIGNMENTS FOR THE OPTICAL ABSORPTION SPECTRA
OF GALLIUM SUBOXIDE ISOLATED IN A KRYPTON MATRIX

<table>
<thead>
<tr>
<th>Peak</th>
<th>λ(A)</th>
<th>(\bar{\nu}(\text{cm}^{-1})^a)</th>
<th>Assignment$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>000</td>
<td>2757</td>
<td>36 226</td>
<td>C(000) + X(000)$^c$</td>
</tr>
<tr>
<td>010</td>
<td>2744</td>
<td>36 444</td>
<td>C(010) + X(000)</td>
</tr>
<tr>
<td>A</td>
<td>2701</td>
<td>37 020</td>
<td>C + X</td>
</tr>
</tbody>
</table>

$^a \pm 15 \text{ cm}^{-1}$.

$^b$ Band energies are taken from band maxima.

$^c (\nu_1, \nu_2, \nu_3)$. 
value for \( v_2 \) seems inordinately large since the average separation in the \( v_2 \) progression of \( \text{Al}_2\text{O} \) is 186 cm\(^{-1}\) which leads one to deduce on the basis of mass considerations alone that the \( v_2 \) value for \( \text{Ga}_2\text{O} \) should be lower than 150 cm\(^{-1}\). However, this increase in the bending mode frequency for \( \text{Ga}_2\text{O} \) may suggest that metal-metal bonding is more important for \( \text{Ga}_2\text{O} \) as opposed to \( \text{Al}_2\text{O} \) in the C excited state since appreciable metal-metal bonding in these molecules should be reflected in a higher value for \( v_2 \) /10,11/. As previously discussed, metal-metal bonding is thought to be important for \( \text{Ga}_2\text{O}, \text{In}_2\text{O}, \) and \( \text{Tl}_2\text{O} \) but not for \( \text{Al}_2\text{O} \) in their respective ground states. The next band denoted by A is assigned to the C + X transition and presumably corresponds to progressions in \( v_1 \) and \( v_2 \), as was observed for \( \text{Al}_2\text{O} \), that are washed out for the \( \text{Ga}_2\text{O} \) molecule.

Figure VI-5 shows the electronic absorption spectrum of \( \text{Ga}_2\text{O} \) isolated in an argon matrix. Table VI-5 lists the assignments corresponding to the band maxima. Only one system was observed which is assigned to the C + X transition that displays two progressions which are assigned to be in the \( v_1 \) and \( v_2 \) modes that have average vibrational separations of 527 cm\(^{-1}\) and 180 cm\(^{-1}\), respectively. The 000-000 transition (labeled 000) is positioned at 2707 Å (36,939 cm\(^{-1}\)) which represents a 713 cm\(^{-1}\) blue shift from the 000 band position in krypton which, again, can be
FIGURE VI-5

ELECTRONIC ABSORPTION SPECTRUM FOR

GALLIUM SUBOXIDE ISOLATED IN AN ARGON MATRIX

$\text{Ga}_2\text{O}:\text{Ar} = 1:4180$
TABLE VI-5
ASSIGNMENTS FOR THE OPTICAL ABSORPTION SPECTRA
OF GALLIUM SUBOXIDE ISOLATED IN AN ARGON MATRIX

<table>
<thead>
<tr>
<th>Peak</th>
<th>$\lambda$(Å)</th>
<th>$\bar{\nu}$(cm$^{-1}$)$^a$</th>
<th>Assignment$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>000</td>
<td>2707</td>
<td>36 939</td>
<td>C(000) + X(000)$^c$</td>
</tr>
<tr>
<td>010</td>
<td>2694</td>
<td>37 121</td>
<td>C(010) + X(000)</td>
</tr>
<tr>
<td>100</td>
<td>2669</td>
<td>37 466</td>
<td>C(100) + X(000)</td>
</tr>
<tr>
<td>110</td>
<td>2656</td>
<td>37 644</td>
<td>C(110) + X(000)</td>
</tr>
</tbody>
</table>

$^a$ ± 15 cm$^{-1}$.

$^b$ Band energies are taken from band maxima.

$^c$ $(\nu_1, \nu_2, \nu_3)$. 
interpreted in terms of the larger polarizability of krypton that induces larger red shifts.

Figure VI-6 shows the laser induced emission spectrum of Ga$_2$O isolated in a krypton matrix with an excitation wavelength of 2660 Å. Table VI-6 lists the corresponding assignments. Emission was observed from two excited states of Ga$_2$O. These two emission systems do not correlate with the system observed in absorption. The emission system labeled B → X has a very intense band origin at 3530 Å (28,328 cm$^{-1}$) which is denoted by 000. The intensity of emission is much larger than that observed from the B state of Al$_2$O. To the red of the 000 band are several other bands labeled "A", "B", "C", "D", and "E". These bands presumably correspond to vibrational progressions in the ground state of Ga$_2$O but the exact interpretation of these progressions is not possible from the information available in this study for two reasons. First, most of these bands are quite broad which causes difficulty in measuring precise band separations that is necessary to interpret the nature of the progressions. Second, these progressions are further obscured by weak overlapping band progressions that perhaps originate from site effects or from "hot bands" of Ga$_2$O in the B state. The A → X emission system is very broad as was noted for the A → X emission of Al$_2$O. Again, this may suggest emission to a repulsive portion of the ground state potential energy
FIGURE VI-6
LASER INDUCED EMISSION SPECTRUM FOR
GALLIUM SUBOXIDE ISOLATED IN A KRYPTON MATRIX

$\text{Ga}_2\text{O:Kr} = 1:1830$

Laser Excitation $\lambda = 2660\text{nm}$
KRYPTON MATRIX

Ga\textsubscript{2}O

A→X

B→X

INTENSITY

cm\textsuperscript{-1} (x 10\textsuperscript{-3})

A
B
C
D
E
### TABLE VI-6

**Assignments for the Optical Emission Spectra of Gallium Suboxide Isolated in a Krypton Matrix**

<table>
<thead>
<tr>
<th>Peak</th>
<th>λ(Å)</th>
<th>(\tilde{\nu}(\text{cm}^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>4854</td>
<td>20 600</td>
<td>A → X</td>
</tr>
<tr>
<td>A</td>
<td>4034</td>
<td>24 792</td>
<td>B → X</td>
</tr>
<tr>
<td>B</td>
<td>3932</td>
<td>25 430</td>
<td>B → X</td>
</tr>
<tr>
<td>C</td>
<td>3833</td>
<td>26 088</td>
<td>B → X</td>
</tr>
<tr>
<td>D</td>
<td>3732</td>
<td>26 797</td>
<td>B → X</td>
</tr>
<tr>
<td>E</td>
<td>3639</td>
<td>27 481</td>
<td>B → X</td>
</tr>
<tr>
<td>000</td>
<td>3530</td>
<td>28 328</td>
<td>B(000) → X(000)</td>
</tr>
</tbody>
</table>

---

**Notes:**

- **a** ± 15 cm\(^{-1}\).
- **b** Band energies are taken from band maxima.
- **c** \((\nu_1, \nu_2, \nu_2)\).
surface. The A state, however, was not observed in absorption as it was for Al\textsubscript{2}O\textsubscript{3} so it is not clear whether the A state of Ga\textsubscript{2}O is bound. Figure VI-9 shows a schematic diagram of all the states observed in emission and absorption.

It is interesting to note for both Al\textsubscript{2}O\textsubscript{3} and Ga\textsubscript{2}O, that the C state was pumped to induce emission, but emission from the C state was only observed for Al\textsubscript{2}O\textsubscript{3}. This suggests that the C state of Ga\textsubscript{2}O radiatively or non-radiatively relaxes much faster than the C state of Al\textsubscript{2}O. This may possibly be correlated with the fact that one would expect much more rapid intersystem crossing to the B state for Ga\textsubscript{2}O as opposed to Al\textsubscript{2}O due to greater spin-orbit coupling. This assumes the proposed triplet multiplicity of the B state is correct.

3. **INDIUM SUBOXIDE**

Figure VI-7 shows the electronic absorption spectrum for In\textsubscript{2}O isolated in a krypton matrix at 15 K, and Table VI-7 lists the corresponding assignments for band maxima. In absorption two band systems were observed. Only the high energy C → X system is shown in Figure VI-7. This system shows a single vibrational progression in the bending mode with an average spacing of 139 cm\textsuperscript{-1} which is smaller than the spacing observed for Ga\textsubscript{2}O as one might expect. Although the band numbering could not
FIGURE VI-7

ELECTRONIC ABSORPTION SPECTRUM FOR
INDIUM SUBOXIDE ISOLATED IN A KRYPTON MATRIX

$\text{In}_2\text{O}:\text{Kr} = 1:725$


### TABLE VI-7

**Assignments for the optical absorption spectra of indium suboxide isolated in krypton and argon matrices**

<table>
<thead>
<tr>
<th>Peak</th>
<th>λ(Å)</th>
<th>$\bar{v}$ (cm$^{-1}$)$^a$</th>
<th>Assignment$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Krypton Matrix**

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A$^d$</td>
<td>3900</td>
<td>25 644</td>
<td>B(000) + X(000)$^c$</td>
</tr>
<tr>
<td>000</td>
<td>3139</td>
<td>31 854</td>
<td>C(000) + X(000)</td>
</tr>
<tr>
<td>010</td>
<td>3125</td>
<td>31 998</td>
<td>C(010) + X(000)</td>
</tr>
<tr>
<td>020</td>
<td>3112</td>
<td>32 132</td>
<td>C(020) + X(000)</td>
</tr>
<tr>
<td>B</td>
<td>3060</td>
<td>32 670</td>
<td>C + X</td>
</tr>
</tbody>
</table>

**Argon Matrix**

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>000$^d$</td>
<td>3058</td>
<td>32 699</td>
<td>C(000) + X(000)</td>
</tr>
<tr>
<td>100$^d$</td>
<td>3005</td>
<td>33 275</td>
<td>C(100) + X(000)</td>
</tr>
</tbody>
</table>

$^a$ ± 15 cm$^{-1}$.

$^b$ Band energies are taken from band maxima.

$^c$ ($v_1$, $v_2$, $v_3$).

$^d$ Not shown in spectra.
be substantiated from the emission studies, it is expected to be accurate in view of the intensity of the 000 band which is assigned to the band origin. The higher energy band denoted by "B" is presumably comprised of higher vibrational numberings in $v_1$ and $v_2$ in analogy with the $C + X$ system of $\text{Al}_2\text{O}$. A single band was assigned to the $B + X$ transition located at 3900 Å (25,644 cm$^{-1}$). The integrated area of this band was about five per cent of the area of the $C + X$ system. $\text{In}_2\text{O}$ is the only molecule that showed a $B + X$ absorption. The spectrum in argon was quite broad; however, a two band system for the $C + X$ transition was observed at 3058 Å (32,699 cm$^{-1}$) and 3004 Å (33,275 cm$^{-1}$) which probably corresponds to a very short progression in $v_1$ with a spacing of 527 cm$^{-1}$.

Figure VI-8 shows the laser induced emission spectrum for $\text{In}_2\text{O}$ isolated in krypton at 15 K with a laser excitation wavelength of 3059 Å. Table VI-8 lists the corresponding assignments to the band maxima. Two band systems are observed in emission and are labeled $B + X$ and $A + X$. The 000 band is tentatively assigned to the band origin of the $B - X$ system and is red shifted by 109 cm$^{-1}$ from the 000 band observed in absorption for the $B + X$ transition of $\text{In}_2\text{O}$. This band is quite intense compared to the $B + X$ emission systems observed for $\text{Al}_2\text{O}$ and $\text{Ga}_2\text{O}$ which is consistent with the fact that this system was observable.
FIGURE VI-8
LASER INDUCED EMISSION SPECTRUM FOR
INDIUM SUBOXIDE ISOLATED IN A KRYPTON MATRIX

$\text{In}_2\text{O:Kr} = 1:712$
Laser Excitation $\lambda = 3059\text{Å}$
<table>
<thead>
<tr>
<th>Peak</th>
<th>$\lambda$ (Å)</th>
<th>$\bar{v}$ (cm$^{-1}$)</th>
<th>Assignment $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 000</td>
<td>5192</td>
<td>19 260</td>
<td>A → X</td>
</tr>
<tr>
<td>3916</td>
<td>25 535</td>
<td>B(000) → X(000) $^c$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ ± 15 cm$^{-1}$.

$^b$ Band energies are taken from band maxima.

$^c$ $(\nu_1, \nu_2, \nu_3)$. 
in absorption for In$_2$O but not for Al$_2$O or Ga$_2$O. As was observed for Al$_2$O and Ga$_2$O, the A $\rightarrow$ X emission is very broad and continuous in character.

D. CONCLUSION

These electronic absorption and laser induced emission experiments show the existence of three electronically excited states for the Group IIIA metal suboxides. Frequencies for the symmetric stretch and bending modes are reported for several of the excited states of M$_2$O. Because of the increased intensity in emission of the B $\rightarrow$ X system in going down the periodic table, it is suggested that the B state may have triplet multiplicity. The ground state symmetric stretching frequency is also reported for aluminum suboxide. In view of the fact that a band corresponding to this frequency is not apparent in infrared spectra, it is suggested that these results indicate Al$_2$O is linear or very nearly so. This result is shown to be consistent with previous thermochemical and mass-spectrometric electron bombardment studies of Al$_2$O.
FIGURE VI-9

SCHEMATIC DIAGRAM OF THE ELECTRONIC STATES

OBSERVED IN ABSORPTION AND EMISSION FOR Al₂O₃, Ga₂O₃,
AND In₂O
TABLE VI-9
LISTING OF THE AVERAGE VIBRATIONAL SPACINGS\textsuperscript{a}
FOR DIFFERENT ELECTRONIC STATES OF THE GROUP IIIA METAL SUBOXIDES ISOLATED IN KRYPTON AND ARGON MATRICES

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>Krypton</th>
<th></th>
<th></th>
<th>Argon</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al\textsubscript{2}O</td>
<td>Ga\textsubscript{2}O</td>
<td>In\textsubscript{2}O</td>
<td>Al\textsubscript{2}O</td>
<td>Ga\textsubscript{2}O</td>
<td>In\textsubscript{2}O</td>
</tr>
<tr>
<td>X</td>
<td>471</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>ν\textsubscript{1}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>482</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>ν\textsubscript{1}</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ν\textsubscript{2}</td>
<td>133</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>C</td>
<td>454</td>
<td>--</td>
<td>--</td>
<td>451</td>
<td>527</td>
<td>576</td>
</tr>
<tr>
<td>ν\textsubscript{1}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>ν\textsubscript{2}</td>
<td>186</td>
<td>218</td>
<td>139</td>
<td>156</td>
<td>180</td>
<td>--</td>
</tr>
</tbody>
</table>

\textsuperscript{a} ± 15 cm\textsuperscript{-1}.

\textsuperscript{b} Symmetric stretching mode.

\textsuperscript{c} Bending mode.
TABLE VI-10

ENERGIES\textsuperscript{a} OF THE EXCITED STATES\textsuperscript{b} OF THE
GROUP IIAI METAL SUBOXIDES ISOLATED IN KRYPTON
AND ARGON MATRICES

| Electronic State | Krypton | | | | | Argon |
|------------------|---------|---------|---------|---------|---------|
|                  | Al\textsubscript{2}O | Ga\textsubscript{2}O | In\textsubscript{2}O | Al\textsubscript{2}O | Ga\textsubscript{2}O | In\textsubscript{2}O |
| Absorption       |         |         |         |         |         |         |
| A                | 23 286  | 25 644  | 37 121  |         |         |         |
| B                |         | 36 444  | 36 226  |         |         |         |
| C                | 36 444  | 36 226  | 31 854  | 37 121  | 36 939  | 32 699  |
| Emission         |         |         |         |         |         |         |
| A                | 24 595\textsuperscript{c} | 20 600\textsuperscript{c} | 19 260\textsuperscript{c} |         |         |         |
| B                | 34 331  | 28 328  | 25 535  |         |         |         |
| C                | 36 233  |         |         |         |         |         |

\textsuperscript{a} ± 15 cm\textsuperscript{-1}.

\textsuperscript{b} Energies correspond to the (000) - (000) transitions unless noted otherwise.

\textsuperscript{c} Band maximum.
REFERENCES


APPENDIX
FIGURE A-1

ADDRESS ASSIGNMENTS FOR THE EVAN'S ASSOCIATES
BOXCAR INTEGRATOR
FIGURE A-2

ADDRESS ASSIGNMENTS FOR THE CONTROL BOARD
OF THE BOXCAR INTEGRATOR