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Reactions and photochemistry of transition metals with hydrogen and methane via matrix isolation FT-IR spectroscopy

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Rice University, 1991
RICE UNIVERSITY

REACTIONS AND PHOTOCHEMISTRY
OF TRANSITION METALS WITH HYDROGEN AND METHANE
VIA MATRIX ISOLATION FT-IR SPECTROSCOPY

By

ZHENGLONG XIAO

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
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DOCTOR OF PHILOSOPHY

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ABSTRACT

Reactions and Photochemistry of Transition Metals with Hydrogen and Methane via Matrix Isolation FT-IR Spectroscopy

By
Zhenglong Xiao

The reactions of transition and main group metals, including Ca, Sc, Ti, V, Cr, Mo, Zn, Ga and Ge, with molecular hydrogen have been investigated using FT-IR matrix isolation spectroscopy. The reactions of gallium with methane in Ar, Kr and pure methane matrices have also been studied.

All the above metals (except Ge) encounter an energy barrier and require photoexcitation to insert into the H-H bond to form MH$_2$. Bond angles for the dihydrides (MH$_2$) of the above metals have been estimated through measured relative intensities of symmetric and asymmetric stretching modes. We have found that CaH$_2$ and ZnH$_2$ are linear (or near linear) molecules, while ScH$_2$, TiH$_2$, VH$_2$, CrH$_2$, MoH$_2$, GaH$_2$ and GeH$_2$ are bent. The stretching force constants for MH$_2$ have been calculated with a diatomic approximation and are found to increase across the row (from Ca to Zn). A correlation between the stretching force constants and the size of the metals and the involvement of 3d electrons in bonding appears to exist. The bent nature of the transition metal dihydrides is also thought to be a consequence of involvement of 3d electrons in bonding.
Monohydrides of V, Mo, Ga, and trihydrides of Sc, Cr, Mo have also been isolated as results of photoreactions of the respective metals with H₂. Formation of polyhydrides (MHₙ, n = 4, 6, etc.) was also observed in the reactions of atomic Ti, and Mo with H₂.

Reactions of metal dimers and trimers with hydrogen have also been observed. Species with terminal hydrogens resulting from the insertion of the dimers of Ca, Sc, Ti, Cr, Ga and Ge into the H-H bond have also been identified as the reaction products of photolysis. Spontaneous reactions of Ga₂ with H₂ yield Ga₂H₂ with two bridging hydrogens. The trimer of gallium is thought to be isolated in Ar matrices and found to react with H₂ to form Ga₃H₂ with two terminal hydrogens upon absorption of UV light.

A ligand-free molecular coordinated dihydrogen complex with the calcium dimer, Ca₂(H₂)₂, was also observed in Kr matrices.

Photolysis with UV light produces methylgallium hydride, CH₃GaH, in the reactions of gallium with methane in Ar, Kr and pure methane matrices.
ACKNOWLEDGMENT

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Finally, my appreciation goes out to the Robert A. Welch Foundation and MSNW, Inc. for their financial assistance throughout this work.
To my wife,

Shumin
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CHAPTER I

INTRODUCTION

1.1. MATRIX ISOLATION SPECTROSCOPY

Matrix isolation spectroscopy, especially infrared spectroscopy, has been a rapidly growing research area\(^\text{(1)}\) and has become a versatile tool in modern chemistry since its discovery in the 1940's. It was first employed by G. N. Lewis\(^\text{(2)}\) in middle 1940's and later advanced by G. Porter\(^\text{(3)}\) and G. Pimentel\(^\text{(4)}\). In its infancy, matrix isolation was principally used by spectroscopists for the purpose of characterizing a particular chemical species (usually short-lived) in terms of its electronic, vibrational and structural parameters. Although matrix isolation still serves as an important tool in this regard, it has grown to include the disciplines of inorganic and organic chemistry with the purpose of delineating reaction sequences and reaction intermediates as well as final products originating from stable reactants. In addition, matrix isolation can also be used for the purpose of modeling room temperature reactions, which are not readily amenable to normal means of analysis.

Matrix isolation is a low temperature beaker\(^\text{(5)}\). It offers a means of preserving a reactive species indefinitely in a rigid host at low temperatures when the species might normally be present only in high temperature vapors or discharges. It also provides a means for studying photochemically generated species as well as weakly bonded species such as molecular species which are fully dissociated under normal conditions of temperature and pressure. The low temperatures needed to condense
the rare gases make it possible to study short-lived species or reaction intermediates at leisure using spectroscopic techniques, since reactions or interactions with other substances in the matrix are prevented (provided that the matrix is at sufficiently high dilution) and thermal decomposition is also minimized.

In addition, matrix isolation can be used alongside a wide variety of the other methods for atmospheric trace gas analysis. Matrix isolation experiments can also help one interpret the processes occurring on the surfaces of interstellar grains or between molecules/atoms/ions in space. It has a wide applicability and the use of infrared spectroscopy offers good selectivity so that many species can be sampled and measured simultaneously. A high sensitivity, precision, and accuracy can be obtained by matrix isolation infrared spectroscopy. And the technique can be extended still further using visible, ultraviolet and Raman, as well as ESR and NMR spectroscopies.

1.2. INTRODUCTION TO REACTIONS OF METALS WITH HYDROGEN

Research in transition metal hydride chemistry is currently moving at a very vigorous pace. Covalent metal hydride complexes have been implicated as intermediates in homogeneous catalytic reactions; ternary metal hydrides are being actively investigated as potential hydrogen storage devices; and the cluster hydride complexes have been synthesized whose cores resemble little fragments of metal with hydrogen atoms attached. Crystallographic methods are extending the limits of accuracy with which hydrogen positions can be determined, and new forms of metal-hydrogen
bonding are being discovered. Chemisorbed hydrogen has been studied extensively on nickel\(^{(7)}\), and palladium\(^{(8)}\) surfaces.

The solid-state transition metal hydrides\(^{(9)}\) are important for their potential applications in energy storage and catalytic applications. In recent years, research on solid-state metal hydrides has led to the discovery of numerous new intermetallic hydrides and also of new phenomena related to the interactions of hydrogen with a metal framework. However, little is known about the analogous in gas phases since they are generally less stable at the high temperatures required for vaporization.

In the last decade, there have been many publications about the activation of H-H and C-H bonds both experimentally\(^{(10)}\) and theoretically\(^{(11)}\), since these are fundamental processes both in homogeneous and heterogeneous hydrogenation catalysis. The activation of the H-H bond by transition metal cations has been extensively investigated by using guided ion beams\(^{(12)}\), ICR\(^{(13)}\). Information such as the reactivities and the bond dissociation energies of M-H\(^{+}\) bonds have been determined.

Transition metal complexes with M-H bonds were first reported in the 1930's\(^{(14)}\). Since then complexes with terminal and bridging M-H bonds have been identified for almost every transition metal. Moleculary coordinated hydrogen complexes which have \(\eta^2\)-H\(_2\) together with other ligands such as CO, PR\(_3\) etc., have been characterized in recent years\(^{(15)}\), where the hydrogen molecule is stably coordinated to a metal center without oxidative addition.

There currently exists an intense interest\(^{(16)}\) in ligand-free transition metal dihydrides, MH\(_2\). For instance, the interaction of dihydrogen with a
single metal atom to give either a molecular dihydrogen complex or an oxidative-addition product is a fundamental step in organometallic and surface chemistry, playing key roles in several homogeneous and heterogeneous catalytic industrial processes. The microscopic reverse, reductive-elimination reaction is of equal importance in understanding of a number of catalytic phenomena involving dihydrogen. The determination of mechanistic details for both forward and backward steps in the model, M + H\textsubscript{2} ↔ MH\textsubscript{2} system presents both experimental and theoretical challenges which impinge on such questions as symmetry-based electronic state correlations, transition states, activation barriers, molecular-electronic structure, and bonding properties.

Metal hydrides are also of importance in astrophysics since hydrogen is a major constituent of space and several hydride species have been detected\textsuperscript{(17)}. The identification of new metal hydrides in the laboratory will help astronomers to identify metal hydride species in solar spectra.

The characterization of metal hydrides is also important in understanding MOCVD (metal organic chemical vapor deposition) processes involving organometallic compounds, since the formation of M-H bonds has been found to play an important role in decomposition of some precursors.

Aggregation reactions of metals to produce dimers and small clusters have been studied experimentally either in low-temperature matrices\textsuperscript{(18)} or in supersonic molecular beams\textsuperscript{(19)} and by quantum mechanics\textsuperscript{(20)}. The interest in small clusters comes, in part, from the connection between isolated clusters and the small metal particles found on the surface of heterogeneous catalysts. A study of the structures and reactivities of
isolated metal clusters may therefore help in understanding some of the reactions which take place on catalytic surfaces. In this study, we have extensively investigated the reactions of first-row transition metal dimers and trimers with molecular hydrogen.

Additionally, matrix isolation infrared spectroscopy provides an excellent method for determining structural and bonding information about neutral transition metal hydrides, such as MH, MH₂, MH₃, etc. The bonding(21) of transition metal atoms has been a great challenge for quantum mechanicians, since it can involve several low-lying atomic states, which are derived from the 4s²3dⁿ, 4s¹3dⁿ+¹, and 4s¹⁴p¹³dⁿ configurations. The “simple” electronic structures of hydride molecules makes them amenable to comparisons of experimental and theoretical results. A detailed understanding of their bonding behavior will be important in further efforts to understand the nature and energetics of bonding in transition metal compounds.

1.3. GENERAL EXPERIMENTS

The multisurface matrix isolation infrared apparatus has been utilized throughout this work, and details of its design have been presented elsewhere(22). The matrix isolation apparatus consists mainly of two chambers. A side view of this set up is shown in Fig. 1-1. The matrix block (Fig. 1-1, a) contains five levels separated with six equally spaced Viton O-rings and sixteen flat surfaces on each level divided with Teflon spacers. A total of sixty surfaces rather than eighty are available for deposition and scanning since some area is used for mounting screws, the silicon
temperature sensor and three quartz crystal microbalances. By rotation and vertical translation of the block with respect to the vacuum shroud, achieved under vacuum, a condensed phase (diluent plus one or more species to be studied) may be deposited on a selected facet. A system of this sort has a rich potential for analytical applications, as well as for synthesis/structural characterization of new molecules.

The matrix block lies on top of the secondary stage of a closed-cycle helium refrigerator (Air Products CSW-202 Displex). The block is coupled to the second stage of the refrigerator with a double ball-bearing mount and a multileaf copper coil which ensures reliable heat transfer and allows a full 360° rotation of the block. A liquid nitrogen dewar (Fig. 1-1, f) is connected to the top of the matrix block with a short length of tubing. Before each experiment, the dewar was filled with liquid nitrogen to help cool down the matrix block from 17 K to ~12 K; this is very essential for hydrogen reaction studies, because the vapor pressure for H₂ is greatly reduced from 17K to 12K. The temperature of the matrix block is measured with a silicon temperature sensor mounted directly on the block. During experiments, liquid nitrogen was periodically added to keep the block temperature as low as possible and as constant as possible. Warming of the matrix from 12K to 17K was achieved by slow vaporization of the liquid nitrogen, usually overnight. The temperature of the matrix block was seen to increase by ~ 0.5°C each day because of the gases trapped. After all the surfaces were used (usually 2 or 3 days), the block was warmed up and cleaned. A gear assembly is attached to the bottom of the jacket which controls rotation of the jacket and resulting rotation of the whole matrix block.
Figure 1-1. Side view of the multisurface FT-IR matrix isolation apparatus.

(a) matrix block;
(b) closed-cycle helium refrigerator;
(c) shutter actuator;
(d) sliding O-ring seal for vertical positioning;
(e) worm gear for matrix block rotation;
(f) liquid-nitrogen dewar;
(g) high temperature furnace;
(h) water-cooled shield;
(i) gate valve between matrix chamber and pump system;
(k) liquid-nitrogen dewar;
(l) water-cooled quartz crystal;
(m) rotating O-ring seal;
(n) electric screwjack for vertical positioning;
(o) liquid-nitrogen dewar;
(p) diffusion pump;
(q) window for furnace temperature measurement;
(r) CsI and polyethylene window sets.
The matrix block is covered with an outer shield which is attached to the first stage of the refrigerator. Four shutters with a window ca. $3/8 \times 5/8$ inch on each of them allow the deposition to happen only on the selected surface. The temperature for the outer shield and the shutters is $\sim 60K$, which keeps the deposition of matrix gases and reactant gases at a minimum.

The IR spectra are recorded by reflecting the focused spectrometer beam off a polished metal surface (rhodium coated copper plate). The spectra were recorded with an IBM-98 FT-IR spectrometer which was interfaced to the matrix chamber through two sets of IR windows (Fig. 1-1, r). One set, the cesium iodide window is for use in the mid-infrared; the other set, the high-density polyethylene window is for the use in far-infrared. The change from one to the other can be made by rotating without losing the vacuum. In a typical experiment, infrared spectra were taken at $1 \text{ cm}^{-1}$ resolution with an average of 100 scans.

The metals were vaporized either from Knudsen cells of different materials or directly from metal filaments (from side chamber, Fig. 1-2, d). The Knudsen cells were enclosed in a tantalum furnace (Fig. 1-1, g). The details of construction of the tantalum furnace can be found in Ball's thesis\textsuperscript{(23)}. The cells and metals were degassed by heating up the furnace to the desired temperature when the matrix block was at room temperature in order to prevent any unwanted deposition on the matrix block. The tantalum furnace is enclosed in a water-cooled shield (Fig. 1-1, h). The furnace assembly is located inside a shield which is cooled with a liquid
Figure 1-2. Top view of the multisurface FT-IR matrix isolation apparatus.

(I) dual light source;
(II) interferometer chamber;
(III) dual sample chamber;
(IV) dual detector chamber;
(V) matrix chamber;
(VI) furnace chamber;
(VII) side furnace chamber;
(VIII) pumping system.

(a) matrix block;
(b) high temperature furnace;
(c) matrix gas inlet (reactant gas inlet immediately below matrix gas inlet);
(d) side furnace (for tube furnace and gas inlet);
(e) matrix gas inlet for side furnace chamber;
(g) fiberoptic UV-VIS source and collector;
(h) gate valve between chamber V and chamber VI;
(i) gate valve between matrix chamber and pumping system;
(k) water-cooled quartz crystal;
(l) windows for photolysis;
(r) CsI and polyethylene window sets.
nitrogen dewar (Fig. 1-1, k). During experiments the liquid nitrogen dewar (Fig. 1-1, k) was filled with liquid nitrogen which served as a trap for water impurities. The shield also rotated and served as a shutter that controls the metal atom flow. The amount of metal vaporizing was controlled by changing the furnace temperature. The temperature of the furnace was measured by either an optical pyrometer (for high temperatures) or by various thermocouples (for low temperatures).

The matrix materials, Ar (99.998%, Matheson), Kr (99.999%, Matheson) were used without further purification. Reaction gases, H₂ (99.9995%, Matheson), D₂ (99.999%, Air Products), and HD (98% isotope, Cambridge Isotope Laboratories) were used as purchased. All the reactant gases and matrix materials were leaked into the matrix chamber through stainless steel needle valves. The amount of matrix material and metal atoms could be determined with use of the quartz crystal microbalance.

The matrix chamber was pumped overnight by a 4 inch oil diffusion pump (Fig. 1-2, VIII) while the matrix block was cooled down and the metal cell was degassed. The background pressure before trapping was typically ~1.0 × 10⁻⁷ Torr as measured using an ionization vacuum gauge. The relative amount of hydrogen was determined from the rise of the matrix chamber pressure due to added hydrogen.

Photolysis was performed with a 100 w medium pressure mercury short arc lamp along with deionized water and long-pass Corning filters. The photolysis time period usually was 10 minutes. The light was shined on the matrix surface through a UV-grade quartz window (Fig. 1-2, l) at an angle of 30°.
In this study, the metal vapors, reactant gases (H₂, HD, D₂, and CH₄, etc.), and an excess of matrix gases (Kr, Ar, and Xe) were deposited on the target simultaneously. Before each trapping, a burst of matrix gas was introduced to the surfaces for a short period of time, ca. 10 seconds, through a 1/8" tubing from the side chamber (Fig. 1-2, VII). This treatment produced an uneven coating of matrix material on the surface and greatly reduced the interferogram in the IR spectrum. An IR reference was recorded right before each trapping experiment. Following each deposition, the IR spectrum was examined to see whether there was a spontaneous reaction. Photochemistry was then carried out by irradiation with light of different energies on each matrix surface during and/or after deposition. Generally, one or more blank experiments were carried out to check the reaction conditions in order to obtain the best results.

1.4. STRETCHING FORCE CONSTANTS AND BOND ANGLES FOR METAL DIHYDRIDES

The identification and characterization of reaction products was made after extensive studies of metal concentration dependency, reactant gas pressure dependency, isotopic labeling and wavelength dependent photolysis. With all the metals investigated in this study, three gaseous hydrogen isotopomers, i.e., H₂, HD and D₂, and also the mixture of H₂ and D₂ have been employed. The naturally occurring isotopes for the metals have very little effect on the observed frequencies of the metal hydrides because differences in the masses of the metal isotopes have a very small effect on the reduced masses. Since metal dihydrides are a common
reaction product for all the metals in this study, a comparison has been made of the stretching force constants and bond angles of MH$_2$ across the series from Ca to Zn.

1.4.1. Stretching Force Constants

The stretching frequencies for MH$_2$, MD$_2$, and MHD have been observed for all the metals. The stretching force constants can be estimated with a diatomic approximation and the stretching frequencies for MHD are utilized assuming the M-H and M-D stretchings of MHD have negligible coupling between each other. The force constants were calculated using the following equations$^{(24)}$:

\[
\begin{align*}
\omega_e^D &= \rho \omega_e^H, \quad \omega_e^D \chi_e^D = \rho \omega_e^H \chi_e^H, \\
\omega^i &= \omega_e^i - 2 \nu_e^i \chi_e^i, \quad \rho = [\mu^H/\mu^D]^{1/2} \\
\text{and} \quad k_{M-H} &= 4\pi^2 (\omega_e^H)^2 \mu^H
\end{align*}
\]  

(1-1)  

(1-2)  

(1-3)

where:  
\(\omega^i\) are the observed frequencies;  
\(\omega_e^i\) are the calculated harmonic frequencies;  
\(\mu^i\) are the reduced masses;  
\(\chi_e^i\) are the anharmonicities;  

and \(k_{M-H}\) is the stretching force constants.

The stretching force constant provides a measurement of the curvature of the potential well near the equilibrium position, and the bond dissociation energy \(D_e\) is given by the depth of the potential energy curve.
Usually the bond becomes stronger as the force constant becomes larger. It is believed that comparison of the force constants should throw some light on the nature of forces holding the atoms together, i.e., the nature of the chemical bonds.

1.4.2. Bond Angles for Metal Dihydrides, MH$_2$

It is generally thought that the bond angle for a triatomic molecule is a good reflection of the hybridization configuration used in the bond formation. For many metal dihydrides it has been possible to obtain a bond angle measurement from the relative intensities of the symmetric and antisymmetric stretching frequencies, where one assumes that the relative transition moments are a vectorial sum of the dipole moment changes of the individual metal-hydrogen bonds. The bond angle can be obtained by using the following relationship$^{(25)}$:

$$\frac{I_{B_2}}{I_{A_1}} = \tan^2 \theta \frac{m_M + 2m_H \sin^2 \theta}{m_M + 2m_H \cos^2 \theta}$$  \hspace{1cm} (1-4)

where: $m_M, m_H$ are the masses of metal and hydrogen; $I_{B_2}, I_{A_1}$ are the relative intensities of the antisymmetric and symmetric stretching modes; and 2$\theta$ is the apical angle.

The uncertainty in measurements of peak intensities and the assumption made for using the above equation is believed to be small and an upper limit of $\pm 5^\circ$ of error in the bond angle calculation is suggested.
1.4.3. Coupling Force Constants \((k_{12})\) for Metal Dihydrides, \(\text{MH}_2\)

1.4.3.1. For bent molecules, \(\text{MH}_2\)

The coupling between the two M-H bonds in \(\text{MH}_2\) can be evaluated by the interaction force constant \(k_{12(\text{MH}_2)}\). The coupling force constants for a bent molecule \(\text{MH}_2\), \(k_{12(\text{MH}_2)}\), can be calculated by using the following equations\(^{(26)}\) with a heavy metal center approximation:

\[
\lambda_1 = \left(1 + \frac{2m_H}{m_M} \cos^2 \theta \right) \frac{k_1 + k_{12}}{m_H} \tag{1-5}
\]

\[
\lambda_3 = \left(1 + \frac{2m_H}{m_M} \sin^2 \theta \right) \frac{k_1 - k_{12}}{m_H} \tag{1-6}
\]

where: \(\lambda_i = 4\pi^2 v_i^2\); and \(k_{12}\) is the coupling force constant.

1.4.3.2. For linear molecules, \(\text{MH}_2\)

The coupling force constants for a linear molecule\((\theta = 90^\circ)\) \(\text{MH}_2\), \(k_{12(\text{MH}_2)}\), can be calculated by using the following equations\(^{(26)}\):

\[
\lambda_1 = \frac{k_1 + k_{12}}{m_H} \tag{1-7}
\]

\[
\lambda_3 = \left(1 + \frac{2m_H}{m_M} \right) \frac{k_1 - k_{12}}{m_H} \tag{1-8}
\]

The calculated values for each individual molecule are listed in discussion part of each chapter and are summarized in Chapter VI.
CHAPTER II

REACTIONS OF SCANDIUM, TITANIUM AND VANADIUM WITH MOLECULAR HYDROGEN

2.1. INTRODUCTION

Compounds containing M-H bonds for early transition metals have only been sporadically studied, despite the extensive interest in their solid state hydrides\(^9\). However, the activation of hydrogen by the early transition metals positive ions, i.e., Sc\(^{+27}\), Ti\(^{+28}\), and V\(^{+29}\), has been extensively studied both experimentally and theoretically\(^{11}\). Armentrout et al\(^{12}\) have investigated the state-specific reaction of atomic transition-metal ions with H\(_2\), D\(_2\), and HD in the gas phase. They claim that for metal ions to react efficiently with hydrogen, a low spin state is essential. They also observed that Ti\(^+\) and V\(^+\) are the only two metal ions which yield nearly equal amounts of MH\(^+\) and MD\(^+\) in HD reactions, and concluded that an MH\(_2\) intermediate was formed. The dissociation energies D\(_e\)(TiH\(^+\)) and D\(_e\)(VH\(^+\)) were found to be 2.39 and 2.03 ev, respectively. The dissociation energy for ScH\(^+\) has been determined to be 2.4 ev by Sunderlin et al\(^{30}\).

Schilling et al\(^{31}\) have calculated the vibrational frequencies for TiH\(^+\) (1696 cm\(^{-1}\)) and VH\(^+\) (1749 cm\(^{-1}\)) and the bond dissociation energies for TiH\(^+\) (2.45 ev) and VH\(^+\) (2.00 ev), which were consistent with the experimental results\(^{29}\). The electronic and geometric structures of ScH\(^+\) and ScH\(_2\)^+ have been studied by ab-initio MCSCF and CI techniques\(^{32}\). ScH\(_2\)^+ was found to be nonlinear with a bond angle of 106.7\(^\circ\), in its \(^1\)A\(_1\) ground state. Large d character in the bond (1.02 3d electrons, or 0.51 3d electron/bond) in
ScH$_2^+$ was found. The dissociation energy for ScH$^+$ was computed to be 2.28 ev, and the first and second Sc-H bond dissociation energies for ScH$_2^+$ were found to be 2.43 and 2.57 ev, respectively.

Schaefer et al$^{33}$ have qualitatively studied the structures of transition metal dihydrides and concluded that TiH$_2$ has a $^3A_1$ ground state and that in its ground state it favors linearity although the potential energy surface is extremely flat with respect to bending. Schaefer et al$^{34}$ also calculated electronic structures and dissociation energies for the family of transition metal tetrahydrides. They predicted the dissociation energies (relative to M + 4H) for TiH$_4$ and VH$_4$ to be 5.72 and 3.73 ev, respectively.

Spectroscopic data$^{35}$ for first row transition metal monohydrides, MH, have been also calculated recently. The predicted ground states for VH and TiH are $^5D$ and $^4F$, respectively, and the dissociation energies for TiH and VH were calculated to be 2.12 ev and 2.30 ev, respectively. The ground states for ScH$^+$ and ScH have been computed$^{32}$ to be $^2\Delta$ and $^1\Sigma^+$, respectively.

In this study, we observed reactions of atoms and dimers of Sc, Ti, and V with hydrogen in Ar and Kr matrices.

2.2. EXPERIMENTAL

Refer to Chapter I for experimental details. Briefly, titanium (99.8%, 0.25 mm diameter, Aldrich Chem. Co.) and vanadium (99.8%, 0.01" diameter, Alfa) were vaporized directly from metal filaments. A schematic of the "tube furnace" used for Ti and V is shown in Fig. 2-1. The vanadium and titanium filaments were heated to the temperature ranges of 1500-1580 and 1380-1460°C, respectively. The oxides on the outside surfaces of the
Figure 2-1. Schematic of the tube furnace for direct vaporization of metals.
metals were removed mechanically prior to heating. The metals were
degassed by slowly heating to the desired temperatures in a separate
chamber and then moved into the matrix chamber for deposition.
Scandium metal (99.5%, Cerac) was vaporized from a molybdenum cell
enclosed in a tantalum furnace over the temperature range 1100 - 1300 °C.
The temperatures were measured with an optical pyrometer. In reactions
of titanium and vanadium, the reactant gases (H₂, D₂, and HD) and the
matrix gases (Kr or Ar) were passed through the furnace and deposited on
the matrix surface.

Potentially, the tube furnace can be used to vaporize refractory second
and third row transition metals, where suitable containers are very hard to
find. As a matter of fact, the tube furnace can be utilized for various
conducting materials, such as TiB₂ fibers, which possess sufficient vapor
pressures below their melting points.

2.3. RESULTS

2.3.1. Scandium-Hydrogen

Fig. 2-2 displays the infrared spectra for reactions of Sc with H₂ in a Kr
matrix. When atomic scandium was cotrapped with an excess of Kr at
12K, it was noted as previously reported(37) that unlike most of the first row
transition metals, Sc spontaneously inserts into the H-OH bond to form
HScOH (where H₂O is present as an impurity). The strong peak at 1472.9
cm⁻¹ in Fig. 2-2(A) is readily assigned to the H-Sc stretching mode for
Figure 2-2. Infrared spectra for reactions of Sc with H₂ in a Kr matrix.

(A) for a freshly trapped matrix;
(B) after photolysis with light of λ > 580 nm for 10 minutes;
(C) after consequent photolysis with UV (320 - 380 nm) light for 10 minutes.
HScOH. No reactions with H₂ were seen upon deposition. The two weak peaks at 1359.6 and 1302.7 cm⁻¹ are thought to be due to a trace amount of unknown impurities, since they are also present in reactions with D₂ and HD. After the matrix surface was photolyzed with light of λ > 580 nm for 10 minutes, several new peaks at 1305.6 (band a), 1354.5 (band b), and 1368.7 cm⁻¹ (band c) were observed. Further photolysis with light other than UV caused no additional change in the IR spectra. Exposure of UV (320 - 380 nm) light to the same matrix, however, produced a new peak at 1294.0 cm⁻¹ and decreased the intensities for peaks at 1305.6 (a), 1368.7 (c) and the peak at 1472.9 cm⁻¹ dramatically. The loss of the the peak for HScOH is due to its decomposition to H₂ and ScO(37). Further photolysis with light of λ > 580 nm was unable to reproduce band a. The differences between the spectra taken before and after photolysis are also shown in Fig. 2-2. It was noticed that bands a and c have the same dependence on photolysis.

Several reactions of Sc with H₂ were carried out in Kr matrices with varied concentrations of Sc atoms and a constant amount of H₂. The resultant infrared spectra are illustrated in Fig. 2-3, where the temperature of the furnace varied from 1180°C to 1250°C. In Fig. 2-3, parts I and II were recorded after photolysis with light of λ > 580 nm and subsequent photolysis with UV (320 - 380 nm), respectively. Apparently, bands a, b, and c result from species containing only one Sc atom. However, band d (at 1294.0 cm⁻¹) was only observed in reactions with higher concentrations of scandium, as seen in Fig. 2-3 (D and E), which strongly suggests that band d is due to a molecule containing the dimer of scandium.
Figure 2-3. A collection of IR spectra for a series of reactions of Sc with H$_2$ in Kr matrices at different concentrations of Sc.

Part I following photolysis with light of $\lambda > 580$ nm for 10 minutes;
Part II following additional photolysis with UV (320 - 380 nm) light for 10 minutes.
where the temperatures for vaporization of scandium are:

(A) 1080°C;
(B) 1120°C;
(C) 1170°C;
(D) 1210°C;
(E) 1250°C.
Fig. 2-4 displays the infrared spectra for the photolytic reactions of Sc with D₂. Bands a, b, and d shift to 948.3, 994.8 and 939.6 cm⁻¹, respectively. A shoulder at 998.5 cm⁻¹ on the peak b is also observed as a result of photolysis with light of λ > 580 nm, as shown in Fig. 2-4(B). The intensities for both peaks at 998.5 (band b) and 994.8 cm⁻¹ were greatly reduced after subsequent photolysis with UV light which caused the loss of bands a, c and the formation of band d in reactions with H₂. It is thought that bands b and c (998.5 cm⁻¹) overlap in reactions with D₂.

Similar reactions with HD were also carried out in a Kr matrix. The resultant IR spectra from reactions with HD are depicted in Fig. 2-5. According to the behavior upon photolysis with different wavelengths, we assign the peaks at 1292.6 and 942.2 cm⁻¹ to band d. As mentioned above, band d is related to the dimer Sc₂ and the Sc-H and Sc-D stretching modes in HD reactions are close in frequencies to those found in reactions with H₂ and D₂, respectively. Since they are in the terminal scandium-hydrogen stretching region. We have assigned band d to a molecule with two terminal hydrogens, Sc₂(t-H)₂.

It is also known from the scandium concentration study that both bands a and b are monoatomic related species. It is noticed in Fig. 2-5 that the peaks at 1348.7 and 967.4 cm⁻¹ for reactions with HD have similar wavelength dependences as band a in H₂ and D₂ reactions. Band a requires with only one H₂ molecule, since in H₂ concentration studies its intensities change slowly with the increase of H₂ pressure. Thus, band a is assigned to scandium dihydride, ScH₂, and band c is assigned to the symmetric stretching mode. The observation of only two bands in the HD studies supports this assignment. The observed frequencies and their
Figure 2-4. Infrared spectra for reactions of Sc with D₂ in a Kr matrix.

(A) for a freshly trapped matrix;
(B) after photolysis with \( \lambda > 580 \) nm for 10 minutes;
(C) after photolysis with UV (320 - 380 nm) light for 10 minutes.
Figure 2-5. Infrared spectra for reactions of Sc with HD in a Kr matrix.

(A) for a freshly trapped matrix;
(B) after photolysis with $\lambda > 580$ nm for 10 minutes;
(C) after consequent photolysis with UV (320 - 380 nm) light for 10 minutes.
assignments are listed in Table 2-1.

Band b in the reactions with HD shifts slightly to 1365.8 and 1356.4 cm\(^{-1}\) in the Sc-H stretching region, and 1009.0 cm\(^{-1}\) in the Sc-D stretching region. Since it was observed that band b has a higher dependence on the concentration of H\(_2\), we assigned this feature to ScH\(_3\). Because only one Sc-H stretching was observed for ScH\(_3\), the geometry for this molecule can not be determined unambiguously. The observed asymmetric stretching is so weak that even if ScH\(_3\) has a pyramidal structure the symmetric stretching may be obscured by the baseline noise. It has been calculated by Jolly et al\(^{38}\) that ScH\(_3\) has a pyramidal geometry with a H-Sc-H angle of 114.0° in its ground state.

It was mentioned above that Sc does not react with H\(_2\) in its ground state which is consistent with theoretical predictions. We observed that ScH\(_2\) was produced upon photolysis with light of \(\lambda > 580\) nm. Since the \(^4\)D \([3d4s(^3\!D)4p]\) state is the only optically active excited state that fall in this range\(^{39}\), we think Sc utilizes dsp hybridized orbitals to form ScH\(_2\). The observation of both symmetric and antisymmetric stretching modes for ScH\(_2\) strongly suggests that it has a nonlinear geometry, which also implies significant involvement of 3d electrons from Sc in bonding with hydrogens.
Table 2-1. Reaction Product Absorptions (cm$^{-1}$) for Reactions of Scandium with Hydrogen in Kr Matrices.

<table>
<thead>
<tr>
<th>observed frequencies(cm$^{-1}$)</th>
<th>tentative assignments</th>
<th>label</th>
</tr>
</thead>
<tbody>
<tr>
<td>1472.9</td>
<td>H-ScOH</td>
<td></td>
</tr>
<tr>
<td>1305.6 ($v_3$), 1368.7 ($v_1$)</td>
<td>ScH$_2$</td>
<td>a</td>
</tr>
<tr>
<td>1365.8,</td>
<td>ScHD$_2$</td>
<td>b</td>
</tr>
<tr>
<td>1356.4,</td>
<td>ScH$_2$D</td>
<td>b</td>
</tr>
<tr>
<td>1354.8</td>
<td>ScH$_3$</td>
<td>b</td>
</tr>
<tr>
<td>1348.7, 967.4</td>
<td>ScHD</td>
<td>a</td>
</tr>
<tr>
<td>1294.0</td>
<td>Sc$_2$H$_2$</td>
<td>d</td>
</tr>
<tr>
<td>1292.6, 942.2</td>
<td>Sc$_2$HD</td>
<td>d</td>
</tr>
<tr>
<td>948.3 ($v_3$), 998.5 ($v_1$)</td>
<td>ScD$_2$</td>
<td>a</td>
</tr>
<tr>
<td>994.8</td>
<td>ScD$_3$</td>
<td>b</td>
</tr>
<tr>
<td>939.6</td>
<td>Sc$_2$D$_2$</td>
<td>d</td>
</tr>
</tbody>
</table>
2.3.2. Titanium - Hydrogen

In titanium reactions, the concentrations of titanium can be controlled by varying the temperature of the filaments or by changing the distance between the filaments and the matrix surface. In this study, we have kept the filament at a fixed distance from the matrix surface to reduce the heat radiation, and have changed the temperature of the filament to achieve different titanium concentrations.

The spectral results of a titanium concentration study are shown in Fig. 2-6. With the temperature of the filament at \(~1380^\circ\text{C}\), no peaks other than those of \(\text{H}_2\text{O}\) and the complex \(\text{Ti:OH}_2^{(37)}\) were observed upon deposition. When the concentration of titanium was increased (the filament temperature was raised to \(~1450^\circ\text{C}\)), two new sharp peaks at 1512.4 and 1396.9 cm\(^{-1}\) were observed. In addition, a broad feature (FWHH=20 cm\(^{-1}\)) centered at 1490 cm\(^{-1}\) became apparent when the concentration of Ti was high. After the matrix was then photolyzed by light with \(\lambda > 520\) nm, the two sharp peaks decreased in intensity together. When the same matrix surface was photolyzed with UV light (280 - 370 nm), they disappeared totally. Due to their appearance only at higher concentrations of Ti, these peaks are thought to result from a spontaneous reaction of \(\text{Ti}_2\) or \(\text{Ti}_3\) clusters with molecular hydrogen. These titanium clusters also react with \(\text{D}_2\) and give two sharp peaks at 1091.7 cm\(^{-1}\) and 1002.8 cm\(^{-1}\), respectively. The broad peak shifted to \(~1080\) cm\(^{-1}\), and was not affected by photolysis at any wavelength. The mechanism for broadening of this feature is not clear. It may suggest that the geometry of this metal cluster hydride is not well defined, or that the molecule rotates in the matrix.
Figure 2-6. Infrared spectra for reactions of Ti with H$_2$ in Kr matrices, at different titanium concentrations.

(I) on newly deposited matrices;

(II) following photolysis with light of $\lambda > 580$ nm for 10 minutes.

where the temperature of titanium filaments was at:

(A) 1380°C;
(B) 1450°C.
Figure 2-7. Summary of infrared spectra for reactions of titanium and hydrogen in Kr matrices. All spectra were recorded after photolysis with light of \( \lambda > 580 \) nm for 10 minutes.

(A) with \( \text{H}_2 \);

(B) with \( \text{HD} \);

(C) with \( \text{D}_2 \).
Extended photolysis with \( \lambda > 520 \) nm light on matrices with a low concentration of titanium produced several new groups of peaks: a doublet at 1412.1 and 1416.5 cm\(^{-1}\), another doublet at 1473.1 and 1477.9 cm\(^{-1}\) and a group of peaks centered at 1657.8 cm\(^{-1}\). These peaks are thought to result from a molecular hydrogen-atomic titanium reaction.

The same experiments have also been carried out with D\(_2\), HD and a mixture of H\(_2\) and D\(_2\) with a ratio of one to one. The spectral results are shown in Fig. 2-7. For D\(_2\) reactions, the two doublets shifted to 1024.5, 1028.1, and 1055.4, 1058.7 cm\(^{-1}\), respectively. The broad band shifted to 1201.4 cm\(^{-1}\). In the HD reactions, only two doublets, one at 1443.0 and 1447.8 cm\(^{-1}\) in the Ti-H stretching region and another at 1039.7 and 1043.0 cm\(^{-1}\) in the Ti-D stretching region were observed. Neither peak was associated with the weaker high frequency peaks as was the case for the H\(_2\) and D\(_2\) reactions. This is readily understood if one assigns the doublets in the H\(_2\) reactions to the symmetric and antisymmetric stretching frequencies of TiH\(_2\), with the less intense one assigned to the symmetric stretching mode. The observation of both symmetric and antisymmetric stretching frequencies indicates that TiH\(_2\) is a bent molecule. All bands for titanium dihydride have been observed to be doublets. This is thought to be due to the effect of different trapping sites. The bending modes for TiH\(_2\) and TiD\(_2\) were detected at 496.1 and 376.5 cm\(^{-1}\), respectively.

A hydrogen concentration study was conducted in Kr matrices, both for H\(_2\) and D\(_2\) and the spectral results are summarized in Fig. 2-8 and Fig. 2-9. In H\(_2\) reactions, the two doublets (1416.5 and 1477.9 cm\(^{-1}\)) always grew together. At low H\(_2\) concentrations, the peaks centered at 1657.8 cm\(^{-1}\) are much weaker relative to the peaks attributed to TiH\(_2\). As the concentration
Figure 2-8. Infrared spectra for titanium reactions with $\text{H}_2$ in Kr matrices, at different hydrogen concentrations. All spectra were recorded after photolysis with light of $\lambda > 580$ nm for 10 minutes.

(A) $[\text{H}_2] = 3.0 \times 10^{-7}$ Torr;
(B) $[\text{H}_2] = 8.0 \times 10^{-7}$ Torr;
(C) $[\text{H}_2] = 2.0 \times 10^{-6}$ Torr;
The image shows a graph with absorbance (arbitrary units) on the y-axis and wavenumber (cm$^{-1}$) on the x-axis. The graph displays three distinct peaks labeled A, B, and C. The peaks are labeled with the species TiH$_4$ and TiH$_2$.
Figure 2-9. Infrared spectra for titanium reactions with D₂ in Kr matrices, at different hydrogen concentrations. All spectra were recorded after photolysis with light of $\lambda > 580$ nm for 10 minutes.

(A) $[D_2] = 1.5 \times 10^{-7}$ Torr;
(B) $[D_2] = 4.0 \times 10^{-7}$ Torr;
(C) $[D_2] = 8.0 \times 10^{-7}$ Torr.
of H₂ increased, the peak at 1657.8 cm⁻¹ was noted to intensify more dramatically than those bands due to TiH₂. This indicates that the peaks centered at 1657.8 cm⁻¹ result from a second species with additional hydrogen, as compared to the TiH₂ molecule. This peak has been tentatively assigned to TiH₄. More obviously, in D₂ reactions, only TiD₂ appeared when the concentration of D₂ was low. And when the pressure of D₂ was increased, the peak at 1201.4 cm⁻¹ became apparent, indicating TiD₄. The observed frequencies are listed in Table 2-2.

In the HD reactions, stretching frequencies for the tentatively assigned TiH₂D₂ were observed at 1656.8 and 1202.2 cm⁻¹. These are seen to be very close to but slightly shifted from the observed stretching frequencies of TiH₄ and TiD₄. Further photolysis with UV (280 - 370 nm) light weakened the intensities for titanium tetrahydride and dihydride. The hydrides can be reversibly produced by photolysis with light of λ > 520 nm. Figure 2-10 shows the reversible photoreactions of Ti with D₂ in a Kr matrix.

The data presented here can not yield an unambiguous structure for titanium tetrahydride. However, a tetrahedron apparently is a reasonable choice. The geometry for TiH₄ in its ground state has been computed by Jolly et al.³⁸ to be tetrahedral with a H-Ti-H angle of 109.5°.

The reactions between Ti and H₂, D₂, HD have also been studied in Ar matrices. In general atomic reaction products appeared to form in less amounts in Ar matrices as compared to Kr matrices. However, the product peaks exhibited the same patterns in Ar matrices as in Kr matrices. In Ar matrices, the ratio of the amounts of TiH₄ and TiH₂ is seen to be larger than that in Kr matrices, most likely because of the lower rigidity and higher mobility of H₂ in an Ar matrix.
Table 2-2. The Observed Frequencies (cm⁻¹) for Titanium Hydrides

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<th></th>
<th>TiH₂</th>
<th>TiD₂</th>
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<td>Ar</td>
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<tr>
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<td>(0.29)</td>
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<td>(2.14)</td>
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<tr>
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<td>1396.9</td>
<td>1002.8</td>
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</tbody>
</table>

*The numbers in parenthesis provide a relative measure of the intensities of the two stretching modes.*
Figure 2-10. Infrared spectra for photoreactions of titanium with D$_2$ in a Kr matrix.

(A) on a newly trapped matrix;
(B) after photolysis with light of $\lambda > 520$ nm for 10 minutes;
(C) after consecutive photolysis with UV light for 10 minutes;
(D) after subsequent photolysis with light of $\lambda > 520$ nm for 10 minutes.
2.3.3. Vanadium - Hydrogen

The observed frequencies for products of the reactions between vanadium and hydrogen are listed in Table 2-3. Figure 2-11 displays the IR spectra for reactions of vanadium with hydrogen in a Kr matrix. On deposition (Fig. 2-11(A)), in addition to the residual H₂O peak and the previously identified water complex V:OH₂(37), a weak feature at 1490.0 cm⁻¹ was also present in the spectrum. Overnight warming of the matrix block from 12K to 17K, caused no additional spectral changes.

After photolyzing the matrix surface with UV light (320 < λ < 380 nm) for 15 minutes, strong peaks at 1490.7 and 1545.2 cm⁻¹ were observed. The peak at 1490.7 cm⁻¹ was observed to be more than 20 times larger than before photolysis. The same matrix surface was then exposed to light with λ > 520 nm, with no significant change in the spectrum, except for a slight increase in the intensities of the peaks listed above. If the matrix was first photolyzed with light λ > 520 nm, all of the above peaks were also present in the spectrum, but with intensities down by a factor of five. We concluded that the ground state of atomic vanadium encounters a barrier with respect to insertion into the H-H bond. The absorption spectra of vanadium atoms in inert gas matrices have been studied by Ford et al(41). In Kr matrices, atomic vanadium has a strong absorption at ~375 nm and a weaker absorption at 471 nm; the coefficients for these two absorption are ~ 6:1, which is close to the ratio of intensities of VH₂ produced by light at the two different wavelengths. The small initial peak at 1490.7 cm⁻¹ in Fig. 2-11(A) is thought to result from the effect of light emitted by the hot vanadium
Table 2-3. The Observed Frequencies (cm\(^{-1}\)) for Vanadium Hydrides

<table>
<thead>
<tr>
<th></th>
<th>(\text{VH}_2)</th>
<th></th>
<th>(\text{VD}_2)</th>
<th></th>
<th>(\text{VHD})</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\text{Kr})</td>
<td>(\text{Ar})</td>
<td>(\text{Kr})</td>
<td>(\text{Ar})</td>
<td>(\text{Kr})</td>
<td>(\text{Ar})</td>
</tr>
<tr>
<td>asym</td>
<td>1490.7</td>
<td>1508.3</td>
<td>1079.5</td>
<td>1092.0</td>
<td>V-H</td>
<td>1518.2</td>
</tr>
<tr>
<td>stretching</td>
<td>(2.29)*</td>
<td></td>
<td>(1.07)</td>
<td>(0.29)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sym</td>
<td>1545.2</td>
<td>1532.4</td>
<td>1111.5</td>
<td>1123.6</td>
<td>V-D</td>
<td>1095.6</td>
</tr>
<tr>
<td>stretching</td>
<td>(0.55)</td>
<td></td>
<td>(0.33)</td>
<td>(0.06)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bending</td>
<td>528.9</td>
<td>386.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>(\text{VH})</th>
<th></th>
<th>(\text{VD})</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1437.4</td>
<td></td>
<td>1046.0</td>
<td></td>
</tr>
</tbody>
</table>

*The numbers in parentheses are integrated peak intensities of the two stretching modes*
Figure 2-11. Infrared spectra for reactions of V with H₂ in a Kr matrix.

(A) on deposition;
(B) following overnight warming;
(C) following photolysis with UV (320-380 nm) light for 15 minutes;
(D) following subsequent photolysis with light of λ > 520 nm for 10 minutes.
filaments during matrix formation. Photolysis with UV (320 - 380 nm) also caused the insertion of V into the H-O bond of water to form HVOH, as seen in Figure 2-11(C).

In the reactions with D₂, the above peaks shifted to 1079.5 and 1111.5 cm⁻¹, respectively. This large shift (1490.7/1079.5 = 1.38) upon reaction with deuterium indicates that the observed bands are due to M-H deformations.

When vanadium reacts with HD, there are two intense sets of peaks, one set lies in the V-H stretching region, and the other in the V-D stretching region, as shown in Fig. 2-12. There were no peaks analogous to the 1545.2 and 1111.5 cm⁻¹ peaks seen in the reactions of H₂ and D₂, respectively. Thus, we conclude that the peaks at 1490.7 and 1545.2 cm⁻¹ in H₂ reactions can be assigned to the antisymmetric and symmetric stretching mode for VH₂ respectively. The peaks at 1079.5 and 1111.5 cm⁻¹ in the D₂ reaction are attributed to the antisymmetric and symmetric stretching for VD₂. The less intense side bands probably represent the same vibrational modes but for different matrix sites. The observation of both symmetric and antisymmetric modes strongly indicates that VH₂ is a bent molecule.

Photolysis with UV light also creates broader peaks at 1437.4 cm⁻¹ and 1046.0 cm⁻¹ for the H₂ and D₂ systems, respectively. These same peaks are present for HD reactions as well. These peaks are thus assigned to vanadium monohydride. The vibrational frequency for gaseous VH was calculated to be 1590.0 cm⁻¹ by Walch et al.⁴². If the anharmonicity (27.6 cm⁻¹, to be described) in taken into account, gaseous VH has a calculated vibrational frequency of 1492.6 cm⁻¹. The gas-phase value can be expected to be greater than the matrix value by ~20 cm⁻¹.
When a mixture of H₂ and D₂ was introduced into the system together, the spectrum was primarily represented by the sum of H₂ and D₂ only reactions. However, peaks at 1095.6 and 1518.2 cm⁻¹ (two major peaks for VHD) also appeared weakly in the spectrum. They were apparently the results of secondary reactions of the monohydrides. The spectra for reactions of vanadium with H₂, D₂, HD and a mixture of H₂ and D₂ are summarized in Fig. 2-12.

The bending frequency for VH₂ was detected in the far-ir region in a Kr matrix using a DTGS (deuterated triglycine sulfate) detector. A peak at 528 cm⁻¹ was only observed after photolysis and was assigned to the bending mode of VH₂. A poor signal to noise ratio in the low frequency region made it difficult to identify a bending frequency for VD₂. However, a peak at 386 cm⁻¹ was only observed after photolysis and was tentatively assigned to the bending frequency for VD₂ which was close to the result 371 cm⁻¹ calculated by applying Teller-Redlich⁴³ product rule.

VH₂ can also be probed in Ar matrices and the frequencies for VH₂, VD₂ and VHD in argon matrices are also listed in Table 2-3. We noted that the intensities of VH₂ peaks in Ar matrices were much smaller than those in Kr matrices. This may result because less H₂ was trapped in Ar than in Kr at the same temperature, or from additional atomic clustering in argon matrices.
Figure 2-12. A collection of IR spectra for reactions of vanadium with hydrogen in Kr matrices after photolysis with UV light for 15 minutes.

(A) with H₂;
(B) with HD;
(C) with D₂;
(D) with a mixture of H₂ and D₂.
2.4. DISCUSSION

Both the symmetric and antisymmetric stretching frequencies of HScH, HTiH and HVH have been identified, which strongly suggests that all dihydrides for Sc, Ti and V are nonlinear molecules. The relative intensities which were obtained from integration of peak areas are listed in Table 2-2 and Table 2-3 together with the frequencies. A bond angle of 110° was obtained for ScH₂. For TiH₂ the bond angle was 147° and 144° in Ar and Kr, respectively. The bond angle for VH₂ was calculated to be 131° in Ar matrices and 127° in Kr matrices. When the relative symmetric and antisymmetric stretching intensities for VD₂ were utilized, the bond angle for VD₂ was 127° in Ar and 125° in Kr matrices, respectively, and for TiD₂, the bond angle was 145° in Ar and 144° in Kr matrices, respectively. The apparent differences of the bond angle in different matrices could result from the differences of polarizabilities of Ar and Kr. The true bond angle values for the respective gas phase species should be closer to those obtained in Ar matrices. The MD₂ values in argon are given as the best estimate of gas phase values since the effects of anharmonicity and matrix interactions are minimized. The related species TiF₂(44) and VF₂(45) have also been found to be bent in matrices. The bond angle of TiF₂ was determined to be 130°. The smaller measured bond angle for VH₂ than TiH₂ confirms a greater involvement of d-orbitals in the metal-hydrogen bond in VH₂. The bent nature for ScH₂ is also thought to result from the participation of 3d orbitals in bonding. For Sc the 3d and 4s orbitals have a comparable radial extent, so the formation of sd-hybrids is energetically feasible. Bauschlicher et al(46) have found that ScH has a \(^1\Sigma^+\) ground state
Table 2-4. Comparisons between H-MD and H-MOH (M = Sc, Ti and V)

<table>
<thead>
<tr>
<th></th>
<th>$\omega_e^H$ (cm$^{-1}$)</th>
<th>$\omega_e^{H_xe}^H$ (cm$^{-1}$)</th>
<th>$k_{M-H}$ (mdyn/Å)</th>
<th>$k_{12}(MH_2)$ (mdyn/Å)</th>
<th>bond angle ($^\circ$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ScD</td>
<td>1363.3</td>
<td>7.29</td>
<td>1.08</td>
<td>0.091</td>
<td>110 ± 5</td>
</tr>
<tr>
<td>H-ScOH</td>
<td>1538.3</td>
<td></td>
<td>1.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-TiD</td>
<td>1416.5</td>
<td>20.45</td>
<td>1.29</td>
<td>0.073</td>
<td>147 ± 5</td>
</tr>
<tr>
<td>H-TiOH</td>
<td>1538.9</td>
<td></td>
<td>1.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-VD</td>
<td>1490.7</td>
<td>27.6</td>
<td>1.44</td>
<td>0.068</td>
<td>131 ± 5</td>
</tr>
<tr>
<td>H-VOH</td>
<td>1583.0</td>
<td></td>
<td>1.47</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
where the Sc-H bond has considerable d-character.

The stretching force constants for HScD, HTiD and HVD have been calculated. The results together with the data obtained from the reactions of Sc, V, Ti with H₂O, are listed in Table 2-4. The force constant is seen to increase from 1.08 mdyn/Å for ScH₂ to 1.44 mdyn/Å in VH₂, which is most likely related to the decrease of atomic radius of the metals. The higher force constant for H-MOH is most likely due to a higher positive charge on the metal which led to a shorter H-M bond length. Table 2-4 also lists the coupling force constants for HMH (M = Sc, Ti, and V).

2.5. SUMMARY

In summary, Sc, Ti, and V have been cotrapped with hydrogen in an excess of Kr or Ar. MH₂ molecules have been observed to be bent for all three metals. The stretching force constant for MH₂ is seen to increase from Sc to V. Possible reactions between Sc, Ti, V and H₂ can be summarized as follows:
\[ M = \text{Sc, Ti, V} \]

\[ M + H_2 \xrightarrow{hv} MH_2 \]
\[ M = \text{Sc} \]

\[ \text{Sc}_2 + H_2 \xrightarrow{UV \ (320 - 380 \text{nm})} \text{Sc}_2H_2 \]
\[ \text{Sc} + 2H_2 \xrightarrow{\lambda > 580 \text{ nm}} \text{ScH}_3 + H \]

\[ M = \text{Ti: } x = 2 \text{ or } 3 \]

\[ \text{Ti}_x + H_2 \xleftrightarrow{12K \ \text{UV (} 270 - 380 \text{ nm})} \text{Ti}_x(t-H)_2 \]
\[ \text{Ti} + 2H_2 \xrightarrow{\lambda > 520 \text{ nm}} \text{TiH}_4 \]

\[ M = \text{V} \]

\[ V + H_2 \xrightarrow{UV \ (320 - 380 \text{ nm})} \text{VH} + H \]
CHAPTER III

REACTIONS AND PHOTOCHEMISTRY OF
CHROMIUM AND MOLYBDENUM WITH MOLECULAR HYDROGEN

3.1. INTRODUCTION

The study of dihydrogen complexes, both in solutions\(^{47}\) and in low temperature matrices\(^{48}\) has been an active area since the first discovery of the complex \([\text{W}(\eta^2-\text{H}_2)(\text{CO})_3(\text{PCy}_3)_2]\) by Kubas et al\(^{49}\). The most studied systems have been complexes of group VI (Cr, Mo, and W) metals which contain \(\eta^2-\text{H}_2\) together with various ligands, such as PR\(_3\), Cp, CO, etc. The \(\eta^2-\text{H}_2\) ligand exhibits characteristic vibrational frequencies around 3000 cm\(^{-1}\), and 600 cm\(^{-1}\). Species \(\text{M(CO)}_5(\text{H}_2)\) (where, \(\text{M} = \text{Cr}, \text{Mo}, \text{and W}\)) have been recently characterized by Turner\(^{50}\). Molecular hydrogen stretching frequencies for \(\text{Cr(CO)}_5(\text{H}_2)\), \(\text{Cr(CO)}_5(\text{HD})\), and \(\text{Cr(CO)}_5(\text{D}_2)\) were observed at 3030 cm\(^{-1}\), 2725 cm\(^{-1}\), and 2242 cm\(^{-1}\), respectively, where the complexes were synthesized through UV photolysis of \(\text{Cr(CO)}_6\) in the presence of \(\text{H}_2\) and its isotopes in liquid Xe solutions at \(-70^\circ\text{C}\).

A lot of attention has also been paid to the ligand free hydrides of Cr and Mo in recent years. Both CrH and MoH have been found\(^{51}\) to have a \(6\Sigma^+\) ground state and have similar d electron populations on the metal centers, i.e., 4.82 and 4.86, respectively. However, CrH (1.72 ev) has a smaller dissociation energy than MoH (2.07 ev). The dissociation energies\(^{52}\) for CrH\(^+\) and MoH\(^+\) are 1.20 ev and 1.40 ev, respectively, which indicates by comparison to the bond energies of neutral species that an electron was
removed from a bonding orbital. The ionic triatomic species\(^{(53)}\), CrH\(_2^+\) and MoH\(_2^+\), have been studied by Goddard et al. They conclude that second row transition metals tend to bond with hydrogen through 4d rather than 5s orbitals and that MoH\(_2^+\) has two equally favorable geometries (\(R_e = 1.705 \text{ Å}, \theta_e = 64.6^\circ\); \(R_e = 1.722 \text{ Å}, \theta_e = 112.3^\circ\)). CrH\(_2^+\) was found to have an open geometry with a bond angle of 107.5\(^\circ\). The dissociation energies \(D_e(\text{HM-H}^+)\) were calculated to be 1.52 and 0.84 ev for MoH\(_2^+\) and CrH\(_2^+\), respectively. More recently, the potential energy surfaces for the reactions of Mo with H\(_2\) have been calculated by Balasubramanian et al\(^{(54)}\). It was found that the excited state Mo\(^{(5D, 4d^5s^1)}\) atom inserts spontaneously into H\(_2\) to form the bent molecule, MoH\(_2\), which has a \(5B_2\) ground state and \(D_e(\text{HMo-H})\) was determined to be 3.29 ev. The bond angle for ground state MoH\(_2\) was found to be 116\(^\circ\). The ground state Mo\(^{(7S)}\) atom has a barrier of 3.86 ev for insertion. Experimentally, Elkind and Armentrout\(^{(55)}\) have examined the reactions of Cr\(^+\) with H\(_2\), D\(_2\), and HD by guided ion beam tandem mass spectroscopy. The bond dissociation energy for CrH\(^+\) was determined to be 1.37 ev.

CrH and CrH\(_2\) have been previously reported as formed by reactions between chromium and hydrogen atoms where the atomic hydrogen was produced by passing molecular hydrogen through a tungsten cell (at \(\sim 2600^\circ\text{K}\)). They were identified with both ESR and IR spectroscopy by Weltner et al\(^{(56)}\). Infrared asymmetric stretching frequencies for CrH\(_2\) and CrD\(_2\) were reported at 1591 cm\(^{-1}\) and 1145 cm\(^{-1}\), respectively. The vibrational frequencies of CrH and CrD in Ar matrices were observed at 1548 and 1112 cm\(^{-1}\). No symmetric stretching frequency for CrH\(_2\) was observed and the bond angle for CrH\(_2\) was uncertain.
In this study, we have found that both Cr and Mo are photoreactive towards molecular hydrogen. CrH₂, and CrH₃ have been identified in the reactions of Cr with H₂ upon photolysis with UV light in both Ar and Kr matrices. Frequencies for species such as MoH, MoH₂, MoH₃, and MoH₄ have been assigned in reactions of Mo with H₂. Both CrH₂ and MoH₂ are found to be bent molecules.

3.2. EXPERIMENTAL

Refer to Chapters I and II for experimental details. In this study, Cr (99.7%, Alfa) was vaporized through an orifice ca. 2 mm from an alumina cell enclosed in a tantalum furnace. Atomic molybdenum was obtained by directly heating Mo (99.97%, 0.25 mm diameter, Aldrich) wires from the side chamber. The temperature ranges for Cr and Mo are 1150 - 1300°C and 2100 - 2300°C, respectively. The temperature was measured with an optical pyrometer.

3.3. RESULTS

3.3.1. Chromium-Hydrogen

In a freshly trapped matrix containing Cr and H₂ in an excess of Kr at 12 K, no indication of spontaneous reactions and formation of a complex Cr(H₂) were observed. Small amounts of water impurity indicated that a previously studied water complex, Cr(H₂O) was formed. After the matrix surface was photolyzed with light of λ > 520 nm, Cr underwent insertion into H₂O to form HCrOH which was indicated by a peak at 1637
cm⁻¹ with no evidence of reactions with H₂. Further photolysis of the same matrix surface with UV light, i.e., 320 - 380 nm, resulted in the observation of a number of intense peaks around 1600 cm⁻¹ (in the H₂O bending region). These peaks must arise from H₂ reactions since they shifted to ca.1170 cm⁻¹ in a D₂ reaction.

Because the Cr-H stretching frequencies happened to be in the bending mode region of H₂O, and H₂O may interfere with the proper assignment for the chromium hydride species, reactions of Cr with D₂ were extensively studied. The IR spectra for a series of reactions with different D₂ concentrations are illustrated in Fig. 3-1.

Spectra in Fig. 3-1(I) were obtained with in situ photolysis with UV (320-380 nm) light, where the system pressure caused by D₂ went from 4.0 × 10⁻⁷ Torr to 2.0 × 10⁻⁶ Torr. Several groups of peaks (labeled a - f ) were observed in different D₂ concentration regions. When the concentration of D₂ was low, only the group a features were present in the spectra, with two peaks at 1180.5 cm⁻¹, and 1160.7 cm⁻¹ (with a shoulder). As the level of D₂ increased, group b peaks at 1150.3 cm⁻¹ and 1169.8 cm⁻¹ became apparent. This strongly suggests that group a peaks result from reactions of a single D₂ molecule and group b from more than one D₂ molecule. Group a was tentatively assigned to chromium dihydride, CrH₂.

Since group b has a higher growth rate with respect to increased D₂ concentrations compared to group a, we conclude that group b is due to the formation of a complex of CrD₂ with a second molecule of D₂, CrD₂(D₂), in which Cr donates electrons to the antibonding orbital of the D-D bond thus slightly weakening the Cr-D bonds and decreasing the stretching frequencies of CrD₂.
Figure 3-1. A summary of IR spectra for the reactions of Cr with D₂, at different D₂ concentrations.

**I** after photolysis with UV (320 - 380 nm) light for 10 minutes.

**II** after additional photolysis with light of 520 - 580 nm for 10 minutes of respective matrices.

(A) \([D₂] = 4.0 \times 10^{-7}\) Torr;

(B) \([D₂] = 6.0 \times 10^{-7}\) Torr;

(C) \([D₂] = 8.0 \times 10^{-7}\) Torr;

(D) \([D₂] = 1.0 \times 10^{-6}\) Torr;

(E) \([D₂] = 2.0 \times 10^{-6}\) Torr;

\(a = \text{CrD}_2; \ b = \text{CrD}_2(D₂)^*; \ c = \text{CrD}_3; \ d = \text{CrD}_3(D₂)^*\).

*the second D₂ molecule is weakly coordinated to CrD₂ or CrD₃.*
The peak labeled as \( c \) at 1097.1 cm\(^{-1} \) was seen to grow as \( D_2 \) concentration increased in a similar manner to \( \text{CrD}_2 \). In those matrices containing higher levels of \( D_2 \), the peak (labeled as \( d \)) at 1099.2 cm\(^{-1} \) became stronger than peak \( c \). Further photolysis with light of 520-580 nm on the same matrix surface enhanced significantly both \( c \) and \( d \) peaks, as shown in Fig. 3-1(II). In the meantime, the intensities of the peaks for group \( a \) and \( b \) decreased. As mentioned above, initial photolysis with light from 520 to 580 nm did not generate these peaks on a freshly trapped matrix, we thus concluded that the increase in intensities for bands \( c \) and \( d \) arose from the excitation of group \( a \) and/or group \( b \) species. However, it was noticed that the peak (\( d \)) at 1099.2 cm\(^{-1} \) grew faster than the peak (\( c \)) at 1097.1 cm\(^{-1} \) when the concentration of \( D_2 \) increased as indicated by the change of relative intensities, we think that peaks \( c \) and \( d \) belong to different species.

Fig. 3-2 shows a summary of the IR spectra for the products which result from the reactions of \( \text{Cr} \) with \( H_2 \) in a Kr matrix. Group \( a \) peaks occurred at 1640.0 and 1606.4 cm\(^{-1} \) and group \( b \) peaks at 1621.4 and 1592.4 cm\(^{-1} \). Peaks \( c \) and \( d \) shifted to 1506.9 and 1510.5 cm\(^{-1} \), respectively. Additional photolysis with 320 - 380 nm light weakened the peaks \( c \) and \( d \) and enhanced peaks due to group \( a \) and \( b \). During this process, the unidentified peak \( e \) exhibited different behavior from any other peaks, which suggests that peak \( e \) belongs to a new species.

A similar series of experiments was also carried out with different HD concentrations. The spectra recorded after photolysis with UV (320 - 380 nm) light and 520 - 580 nm light are shown in Fig. 3-3(I) and (II), respectively. \( \text{CrHD} \) (group \( a \)) has two sets of peaks, one set in the Cr-H stretching region at 1627.1 cm\(^{-1} \) and 1617.0 cm\(^{-1} \) and the other in the Cr-D
Figure 3-2. IR spectra for the photoreactions of Cr with H₂ in a Kr matrix.

(A) on a freshly trapped matrix;
(B) after photolysis with UV (320 - 380 nm) light;
(C) after photolysis with light of 520 - 580 nm on the same surface;
(D) after additional photolysis with UV (320 - 380 nm) light on the same surface.

\[ a = \text{CrH}_2; \quad b = \text{CrH}_2(\text{H}_2); \quad c = \text{CrH}_3. \]
Figure 3-3. A summary of IR spectra for the reactions of Cr with HD in Kr matrices at different HD concentrations.

(I) after photolysis with UV (320-380 nm) light for 10 minutes.
(II) after additional photolysis with light of 520 - 580 nm for 10 minutes.

(A) \([\text{HD}] = 4.0 \times 10^{-7} \text{ Torr} \);
(B) \([\text{HD}] = 7.0 \times 10^{-7} \text{ Torr} \);
(C) \([\text{HD}] = 1.0 \times 10^{-6} \text{ Torr} \);

\(\text{a} = \text{CrHD}; \text{ b} = \text{CrHD(HD)}; \text{ c} = \text{CrH}_2\text{D, CrHD}_2.\)
stretching region at 1174.4 cm\(^{-1}\) and 1167.4 cm\(^{-1}\). The complex (group b), CrHD(HD), has frequencies at 1607.1 and 1160.7 cm\(^{-1}\). As seen in Fig. 3-3(II), in addition to the groups mentioned above, photolysis with light of 520 - 580 nm which typically created groups c and d peaks gave three peaks in the Cr-H stretching region at 1510.7, 1507.6 cm\(^{-1}\) and 1563.5 cm\(^{-1}\), and two peaks in the Cr-D stretching region, at 1099.2 cm\(^{-1}\) and 1124.3 cm\(^{-1}\). Also, one notices that as the concentration of HD increased, the relative intensities of peaks at 1124.1 and 1099.2 cm\(^{-1}\) changed and that a new peak at 1099.2 cm\(^{-1}\) overlaps with the peak at 1097.1 cm\(^{-1}\) which was seen in the reactions with lower HD levels.

A collection of IR spectra for reactions products of Cr with H\(_2\), D\(_2\), HD and a mixture of H\(_2\) and D\(_2\) are shown in Figures 3-4 and 3-5. The two peaks at 1563.5 and 1124.1 cm\(^{-1}\) are present in both reactions with HD and mixtures of H\(_2\) and D\(_2\) as shown in Fig. 3-5 which strongly indicates that this molecule involves more than one hydrogen molecule. A reasonable assignment for this species (group c) is chromium trihydride, CrH\(_3\), and group d is tentatively assigned to a weak complex of CrH\(_3\) with H\(_2\). In the experiments with HD or mixtures of H\(_2\) and D\(_2\), one expects two isotopomers for chromium trihydride, i. e., CrH\(_2\)D and CrHD\(_2\), where CrH\(_2\)D has frequencies closer to CrH\(_2\) and CrHD\(_2\) has frequencies adjacent to CrH in the Cr-H stretching region.

Without direct observations of the bending modes for CrH\(_3\), the geometry of CrH\(_3\) can not be determined unambiguously. However, if only the stretching modes are taken into consideration, a planar structure is proposed for the following reasons. In a planar geometry, CrH\(_3\) belongs to
Figure 3-4. A collection of IR spectra for the reactions of chromium with hydrogen in Kr matrices after photolysis with UV light for 10 minutes.

(A) with H₂;
(B) with HD;
(C) with D₂;
(D) with a mixture of H₂ and D₂.
Figure 3-5. A collection of IR spectra for the reactions of chromium with hydrogen in Kr matrices, after consecutive photolysis with UV light and light of 520 - 580 nm for 10 minutes.

(A) with H₂;
(B) with HD;
(C) with D₂;
(D) with a mixture of H₂ and D₂.
$D_{3h}$ group for which there is only one ($v_3$) stretch is IR active bond stretching mode. Additionally, when one of the H's is replaced by D, the symmetry is lowered to $C_{2v}$ in which all the normal modes are IR active including two stretching modes, $v_3$ and $v_1$, in the Cr-H stretching region for CrH$_2$D. The antisymmetric mode is expected to be very similar to the one infrared active mode of CrH$_3$, and the frequency at 1510.7 cm$^{-1}$ can be assigned to the antisymmetric mode for CrH$_2$ moiety of CrH$_2$D. The Cr-H stretching mode in CrD$_2$H, on the other hand seems likely to be responsible for the peak at 1563.5 cm$^{-1}$. Alternatively, this peak could be assigned to the the symmetric stretching mode of the CrH$_2$ group in CrH$_2$D. This mode should, however, be much weaker than the antisymmetric mode. We thus prefer to assign the 1563.5 cm$^{-1}$ peak to the Cr-H stretching mode in CrD$_2$H, which is close to the previously reported vibration frequency of CrH$^{(56)\text{.}}$. A similar assignment can be made for assignments of the Cr-D modes as shown in Table 3-1. The observed peaks can be assigned to stretchings of CrH$_2$D and CrHD$_2$.

In the study with different concentrations of D$_2$, it was noticed that CrD$_3$ was not formed in those matrices with low D$_2$ concentrations. Additionally, because initial photolysis with light of $\lambda > 520$ nm did not produce CrH$_3$, we conclude that CrH$_2$ and the group b species, i.e. the complex, CrH$_2$(H$_2$), are the precursors for chromium trihydride. Likely geometries for CrH$_2$(H$_2$) involve either a side-on or an end-on bonded dihydrogen as shown:
The excitation of CrH$_2$(H$_2$) by light of 520 - 580 nm can apparently promote electrons from Cr to the antibonding orbital of H-H causing the breakage of the H-H bond and the formation of a third Cr-H bond, according the following reactions:

\[
\text{CrH}_2(\text{H}_2) \xrightarrow{\lambda > 520 \text{ nm}} \text{UV}(320-380\text{ nm}) \xrightarrow{} \text{CrH}_3 + \text{H}
\]

As shown in Fig. 3-2, the above reaction is also to some degree photoreversible.

The results of a series of experiments with the same H$_2$ level, but different chromium concentrations, are summarized in Fig. 3-6, where the temperature of the furnace was varied from 1160°C to 1300°C. During this experiment, a small amount of D$_2$ was intentionally added to form CrD$_2$, and the intensities for CrD$_2$ stretchings were used as an internal relative standard with respect to other peaks. No spontaneous reactions due to atomic Cr or diatomic Cr$_2$ with H$_2$ were observed. The previous described groups a, b, c and d peaks are all seen to show similar variation with respect to the Cr concentration and are all thought to result from reactions of atomic Cr. From this study, peak e appears to contain only one Cr atom. As shown in Figure 3-6, when the concentration of Cr was high, in addition to the above groups, a broad peak (f) at 1375 cm$^{-1}$ was observed, which was amplified by further photolysis with 520 nm < $\lambda$ < 580 nm. The above peak
Table 3-1. The Observed Frequencies (cm\(^{-1}\)) for Chromium Hydrides

<table>
<thead>
<tr>
<th></th>
<th>CrH(_2)</th>
<th>CrD(_2)</th>
<th>CrHD</th>
<th>CrH(_3)</th>
<th>CrD(_3)</th>
<th>CrH(_2)D</th>
<th>CrHD(_2)</th>
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<tr>
<td></td>
<td>Kr</td>
<td>Ar</td>
<td>Kr</td>
<td>Ar</td>
<td>Kr</td>
<td>Ar</td>
<td></td>
</tr>
<tr>
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<td></td>
<td></td>
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</tr>
<tr>
<td>stretching</td>
<td></td>
<td></td>
<td>(2.17)*</td>
<td>(0.26)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>symmetric</td>
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<td>1180.5</td>
<td>1189.1</td>
<td>Cr-H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>stretching</td>
<td></td>
<td></td>
<td>(0.81)</td>
<td>(0.09)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cr-D</td>
<td>1167.4</td>
<td>1174.4</td>
<td>1172.0</td>
<td>1185.0</td>
</tr>
</tbody>
</table>

*The numbers in parentheses provide a relative measure of the intensities of the two stretching modes.*
Figure 3-6. A summary of IR spectra for the reactions of Cr with $H_2$ (with $D_2$, $[H_2] : [D_2] = 10 : 1$), at different Cr concentrations. All spectra were recorded after 10 minutes exposure of UV (320 - 380 nm) light (I) and light of 520 - 580 nm (II).

where the temperature of the furnace was at:

(A) 1160°C;
(B) 1190°C;
(C) 1215°C.
(D) 1248°C
(E) 1275°C
(F) 1300°C.
shifted to 1000 cm\(^{-1}\) in the reactions with D\(_2\). Since these peaks are observed only in reactions with a high concentration of Cr, it is tentatively assigned to a diatomic Cr\(_2\) reaction product. Because the observed frequency is in the region of terminal Cr-H stretching mode, group \(f\) is tentatively assigned to a HCrCrH molecule. It might also thought as a weakly interacting dimer of CrH where the hydrogens are partially bridging.

Reactions of Cr with H\(_2\) and D\(_2\) were also carried out in Ar matrices. The results are shown in Fig. 3-7 and are found to be very similar to those in Kr matrices except for slight frequency shifts. As was the case in Kr, two peaks at 1513 and 1509 cm\(^{-1}\) appeared after consecutive photolysis with UV(320 - 380 nm) light and light of 520 - 580 nm in reactions with H\(_2\). The corresponding peaks in the reactions with D\(_2\) were observed at 1106.4 and 1098.5 cm\(^{-1}\). This splitting is due to either complexation or slight change in the geometry for CrH\(_3\). The observed frequencies in both Kr and Ar matrices and their tentative assignments are summarized in Table 3-2.
Figure 3-7. IR spectra for the reactions of Cr with H₂ and D₂ in Ar matrices, after consecutive photolysis with UV (320 - 380 nm), and 520 - 580 nm light.

(A) H₂ reactions;

(B) D₂ reactions.
Table 3-2. Reaction Product Absorptions (cm\(^{-1}\)) for Reactions of Chromium with Hydrogen in Kr and Ar Matrices.

<table>
<thead>
<tr>
<th>obs. frequencies (cm(^{-1}))</th>
<th>Kr</th>
<th>Ar</th>
<th>assignments</th>
<th>label</th>
</tr>
</thead>
<tbody>
<tr>
<td>1640.0, 1606.4</td>
<td>1614.9, 1651.3</td>
<td>CrH(_2)</td>
<td></td>
<td>a</td>
</tr>
<tr>
<td>1621.4, 1592.4</td>
<td></td>
<td>CrH(_2)(H(_2))</td>
<td>b</td>
<td></td>
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<tr>
<td>1627.1, 1617.0, 1174.4, 1167.4</td>
<td>1635.7, 1617.5, 1185.0, 1172.0</td>
<td>CrHD</td>
<td></td>
<td>a</td>
</tr>
<tr>
<td>1563.5, 1099.1, 1097.1</td>
<td></td>
<td>CrHD(_2)</td>
<td></td>
<td>c</td>
</tr>
<tr>
<td>1510.7, 1124.1</td>
<td></td>
<td>CrH(_2)D</td>
<td></td>
<td>c</td>
</tr>
<tr>
<td>1506.9</td>
<td></td>
<td>CrD(_2)</td>
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<td>a</td>
</tr>
<tr>
<td>1510.5, 1506.9</td>
<td>1513.0, 1509.0</td>
<td>CrH(_3)</td>
<td></td>
<td>c</td>
</tr>
<tr>
<td>1180.5, 1160.7</td>
<td>1167.2, 1189.1</td>
<td>CrD(_2)(D(_2))</td>
<td>b</td>
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<td>1169.8, 1158.5</td>
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<td>CrHD(HD)</td>
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<td>b</td>
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<tr>
<td>1607.1, 1160.7</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1099.1, 1097.1</td>
<td>1106.4, 1098.5</td>
<td>CrD(_3)</td>
<td></td>
<td>c</td>
</tr>
<tr>
<td>1375.0</td>
<td></td>
<td>HCrCrH, H-CrCrD</td>
<td>f</td>
<td></td>
</tr>
<tr>
<td>1000.1</td>
<td></td>
<td>DCrCrD, D-CrCrH</td>
<td>f</td>
<td></td>
</tr>
<tr>
<td>1328.0</td>
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<td>e</td>
<td></td>
<td>e</td>
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</table>
3.3.2. Molybdenum-Hydrogen

3.3.2.1. Reactions of Mo with H₂, D₂, and HD

The IR spectrum of a newly deposited Kr matrix containing Mo and molecular hydrogen exhibits two new peaks at 1709.3 cm⁻¹ and 1743.3 cm⁻¹. The intensities of the above two peaks were enhanced significantly upon photolysis with UV, i.e., 320 - 380 nm light. The IR spectra for the products of reactions between Mo and H₂, D₂, HD after UV photolysis are shown in Fig. 3-8. One sees that the above two peaks undergo a large shift to 1227.2 and 1250.6 cm⁻¹ upon reaction with D₂. Similar experiments with HD gave a doublet in the Mo-H stretching region, at 1720.0, 1732.2 cm⁻¹; in the Mo-D stretching region, a doublet at 1243.4 and 1234.7 cm⁻¹ was observed.

Besides the above peaks which can be readily assigned to the symmetric and antisymmetric stretching modes for MoH₂, additional peaks with much smaller intensity at 1674.1 cm⁻¹ in H₂ reactions and at 1202.2 cm⁻¹ in the D₂ reaction were also observed. These two peaks were also presented in the reactions with HD at the exactly same frequencies. They were thus assigned to molybdenum monohydride, MoH. The vibrational frequency (ωₒ) for the ground state MoH(⁶S⁺) was recently calculated by Langhoff et al(51) to be 1662 cm⁻¹, which agrees reasonably well with our experimental result.

A series of experiments with different hydrogen concentrations was carried out in Kr matrices where the temperature of the Mo wires was kept at ~2150°C. The resulting IR spectra are shown in Fig. 3-9. In the
Figure 3-8. IR spectra for reactions of molybdenum with hydrogen in Kr matrices. All spectra were recorded after photolysis with UV (320 - 380 nm) light for 10 minutes.

(A) with H₂;
(B) with HD;
(C) with D₂;
(D) with a mixture of H₂ and D₂.
Figure 3-9. IR spectra for a series of reactions of Mo with H$_2$ in Kr matrices, with different H$_2$ concentrations.

(A) [H$_2$] = $4.0 \times 10^{-7}$ Torr;
(B) [H$_2$] = $8.0 \times 10^{-7}$ Torr;
(C) [H$_2$] = $1.0 \times 10^{-6}$ Torr.
reactions with higher concentration of hydrogen, there appears to be an extra peak at 1849.2 cm\(^{-1}\), which was not present in spectra with low H\(_2\) concentrations. In the reactions with D\(_2\) the analogous peak is found at 1355.5 cm\(^{-1}\). Because this peak was only apparently observed in the experiments with high H\(_2\) concentrations, it was assigned to the stretching modes of molybdenum tetrahydrides, MoH\(_4\). In the reactions with HD, the Mo-H and Mo-D stretchings of MoH\(_2\)D\(_2\) were detected at 1850.8 and 1355.5 cm\(^{-1}\), respectively.

3.3.2.2. Photochemistry of Mo and H\(_2\)

The atomic absorption spectrum of Mo is dominated by two strongly allowed transitions\(^{58}\). These transitions (\(a^7S\rightarrow z^7P_0, a^7S\rightarrow y^7P_0\)) have been observed by several groups to occur in pure Kr matrices at \(\sim 350\) and \(\sim 300\) nm, respectively.

After molybdenum was cotrapped with H\(_2\) in Kr, the matrix surface was exposed to light of different wavelengths. Photolysis with light other than UV light caused no changes in the spectra. However, after the matrix surface was photolyzed with UV light (320 - 380 nm), the peaks which were assigned to molybdenum dihydride enhanced dramatically. The intensities after photolysis are about three times stronger than those before photolysis. This suggests that a barrier does exist for the insertion of ground state atomic Mo into the H-H bond, which is in agreement with recent theoretical predictions\(^{54}\). The presence of small amount of molybdenum dihydrides in those spectra taken just after trapping may either result from the
reactions of long lived excited states of molybdenum or from reactions of hydrogen atoms formed at the hot Mo filaments (at ~2200°C).

Following photolysis with light of \(\lambda > 400\) nm for 15 minutes on the same matrix, the peaks for MoH\(_2\) were seen to decrease in intensities as shown in Fig. 3-10. After two-hour photolysis with light of \(\lambda > 400\) nm, the dihydride is almost lost. Meanwhile the peak at 1849.0 cm\(^{-1}\) which was tentatively assigned to MoH\(_4\) has grown significantly. Molybdenum dihydride, MoH\(_2\), was reproduced by subsequently photolyzing the matrix surface with UV (320-380 nm) light for 10 minutes. This suggests that photoexcitation with light of \(\lambda > 400\) nm of MoH\(_2\) populates an electronic state which can react with second molecule of hydrogen to form MoH\(_4\). The reaction also seems to be photoreversible as:

\[
\text{MoH}_2 + \text{H}_2 \xrightleftharpoons[\text{UV}(320-380\text{ nm})]{\lambda > 400\text{ nm}} \text{MoH}_4
\]

The reverse reaction may be similar to the known photoinduced reductive-elimination of H\(_2\) from \((\eta^5\text{-C}_5\text{H}_5)_2\text{MoH}_2\)\(^{(59)}\). The resultant IR spectra of the products for the reactions with H\(_2\) and D\(_2\) are summarized in Fig. 3-10 and Fig. 3-11, respectively.

It is also interesting to note that when a matrix which contains the MoH\(_2\) product is irradiated with light of 270 - 320 nm for 10 minutes, MoH\(_2\) is totally removed and MoH\(_2\) is not reproduced by photolysis with 320 - 380nm light. It seems likely that the more energetic light (270 - 320 nm) may excite MoH\(_2\) to a high lying dissociative electronic state which gives sufficient energy to the molecular hydrogen to cause it to be ejected out of
Figure 3-10. A summary of IR spectra for the reactions and photochemistry of Mo with H₂ in a Kr matrix.

(A) a freshly trapped matrix;
(B) after photolysis with UV (320 - 380 nm) light for 10 minutes;
(C) following photolysis with λ > 400 nm for 15 minutes;
(D) following photolysis with UV (320 - 380 nm) light for 10 minutes.
Figure 3-11. A summary of IR spectra for the reactions and photochemistry of Mo with D₂ in a Kr matrix.

(A) a freshly trapped matrix;
(B) after photolysis with UV (320 - 380 nm) light for 10 minutes;
(C) following photolysis with λ > 400 nm for 15 minutes;
(D) following photolysis with UV (320 - 380 nm) light for 10 minutes.
the matrix cage. Spectra for different sets of photolysis of a matrix of Mo and H$_2$ in excess of Kr are shown in Fig. 3-12.

As shown in Fig. 3-13, after UV photolysis of a matrix of Mo and H$_2$, the peak due to MoH (at 1674.1 cm$^{-1}$) vanished and a new peak at 1680 cm$^{-1}$ became apparent. In the HD reactions, there were two peaks at 1676.0 and 1685.7 cm$^{-1}$ which were also observed in the reaction with a mixture of H$_2$ and D$_2$. They were tentatively assigned to stretching modes of molybdenum trihydride, MoH$_3$, for the same reasons as in the reactions of chromium with hydrogen. The formation of MoH without any photolysis may result from reactions of Mo with H atoms produced by the hot Mo filaments. In the reaction of Cr with H$_2$, the peaks due to CrH$_3$ were much stronger than those assigned to MoH$_3$ in reactions of Mo with H$_2$. This is not unexpected, because Cr favors the +3 oxidation state while Mo favors higher oxidation states such as +4 and +6.

Finally we have noted that weak peaks after photolysis of $\lambda > 400$ nm light are observed, as shown in Fig.3-10(C), in the neighborhood of 1961cm$^{-1}$ in H$_2$ reactions and a group of peaks around 1412 cm$^{-1}$ in D$_2$ reactions. They appeared at a higher frequencies than those peaks previously assigned MoH$_4$. This suggests that they may be due to a higher hydride such as molybdenum hexahydride, MoH$_6$.

In order to observe the effect of the matrix on the above chemistry, we have also investigated Mo and H$_2$ reactions in an argon matrix. The results appeared to closely resemble those for a krypton matrix. Assignments and observed frequencies in both Ar and Kr matrices are given in Table 3-3 and 3-4.
Figure 3-12. A collection of IR spectra for the reactions and photochemistry of Mo with H₂ in a Kr matrix.

(A) a freshly trapped matrix;
(B) after photolysis with UV (320 - 380 nm) light for 10 minutes;
(C) following photolysis with light of 270 < λ < 320 nm for 15 minutes;
(D) following photolysis with UV (320 - 380 nm) light for 10 minutes.
Figure 3-13. Portion of IR spectra for the reactions of Mo with hydrogen in Kr matrices.

(Ι) Spectra from the freshly deposited matrices;
(ΙΙ) Spectra taken after 10-min photolysis with UV (320-380 nm) light.

(A) with H₂;
(B) with HD;
(C) with D₂;
(D) with a mixture of H₂ and D₂.
Table 3-3. The Observed Frequencies (cm\(^{-1}\)) for Molybdenum Hydrides

<table>
<thead>
<tr>
<th></th>
<th>MoH(_2)</th>
<th></th>
<th>MoD(_2)</th>
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<th>MoHD</th>
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<td>Ar</td>
<td>Kr</td>
<td>Ar</td>
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<td>asym</td>
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<tr>
<td></td>
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<td>(4.00)</td>
<td>(0.50)</td>
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<table>
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<tr>
<th></th>
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<tr>
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<td>1202.8</td>
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<tr>
<th></th>
<th>MoH</th>
<th>MoD</th>
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<tbody>
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<td>1675.4</td>
<td>1202.0</td>
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*The numbers in parentheses provide a relative measure of the intensities of the two stretching modes.*
Table 3-4. Reaction Product Absorptions (cm\(^{-1}\)) for Reactions of Molybdenum with Hydrogen in Kr and Ar matrices.

<table>
<thead>
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<th>obs. frequencies (cm(^{-1}))</th>
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<td>MoH</td>
</tr>
<tr>
<td>1709.3, 1743.1</td>
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<td>1680.0</td>
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<td>1849.2</td>
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<td>1961</td>
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<td>1850.8, 1355.5</td>
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<td>1676.2, 1215.3</td>
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<td>1685.9, 1202.8</td>
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<tr>
<td>1720.0, 1732.2, 1234.7, 1243.4</td>
<td>1732, 1745, 1239, 1252</td>
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<tr>
<td>1202.0</td>
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<td>1227.2, 1250.6</td>
<td>1234.0, 1257.8</td>
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<td>1412</td>
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3.4. DISCUSSION

Both CrH$_2$ and MoH$_2$ are bent molecules since the symmetric and antisymmetric stretching modes have been identified. The bond angle for chromium dihydride has been calculated to be 118° in both Ar and Kr matrices. In this case the relative intensities for CrD$_2$, rather than those for the CrH$_2$ stretching frequencies have been used since interference due to H$_2$O bending mode occurs for CrH$_2$. The bond angle for molybdenum dihydride is calculated to be 110° in a Kr matrix by using the intensities of both MoH$_2$ and MoD$_2$. In an Ar matrix, the bond angles for MoH$_2$ and MoD$_2$ were calculated to be 108° and 114°, respectively. It is thought that the variation of the bond angle mainly arise from the inaccuracy in measurements of the area of weak peaks rather than the effects of matrices. In any cases, the measured derivation of the bond angle is within ±5°. The geometry of CrH$_2$ has been studied theoretically using FSGO calculations by Simons et al.(60). The bond angle of CrH$_2$ was predicated to be 103.1° which was interpreted in terms of negatively charged hydrogens which repel each other and open up the bond angle. This work suggests the bond angle for CrH$_2$ is larger than the calculated value. The bond angle for MoH$_2$ was calculated by Balasubramanian et al.(54) to be 116° with MoH$_2$ in a $^5B_2$ ground state, which is slightly higher than our reported experimental value.

Both CrH$_2$ and MoH$_2$ have been shown to be highly bent molecules with MoH$_2$ slightly more bent than CrH$_2$. This suggests that d electrons are strongly involved in the bonding for both Cr and Mo. The slightly smaller bond angle for MoH$_2$ may be explained by the increased tendency to use 4d
electrons for second row transition metals in bonding\cite{53}. Recently, the spectroscopic properties and potential energy curves of MoH and MoH\(^+\) have been investigated theoretically by K. Balasubramanian et al\cite{61}. They found that Mo-H bonds have considerable d character both in the neutral and ionic species.

It is interesting to note in Fig. 3-4, and Fig. 3-8 that both CrHD and MoHD are observed as doublets rather than the expected single peaks in the M-H and M-D stretching regions. This can not be explained as resulting from two different matrix sites, since a similar splitting was not observed for CrH\(_2\) and MoH\(_2\). We believe that the doublets are best explained by a slight derivation from a symmetric structure for CrHD and MoHD. It is not known whether this structure only applies to the MHD species or whether it applies to the MH\(_2\) species as well. If such a structure exists, it implies the existence of a double minimum in the metal hydrogen bonds in the Cr and Mo triatomic hydrides. This situation which has not previously been noted for any other XY\(_2\) triatomic species. A similar phenomenon was also seen in the GeH\(_2\):OH\(_2\) complex by Andrews et al\cite{62}.

The stretching force constants for the monohydrides, MH, of Cr and Mo, have been calculated to be 1.51 and 1.75 mdyn/Å, respectively. The stretching force constants for the dihydrides, MH\(_2\), were calculated from frequencies for the HMD species where the MH and MD bonds are treated as independent uncoupled vibrations. A diatomic approximation was used to correct for anharmonicity. The stretching force constants were found to be 1.64 and 1.86 mdyn/Å for CrH\(_2\) and MoH\(_2\), respectively. The larger stretching force constants for MoH and MoH\(_2\) than that for CrH and CrH\(_2\)
Table 3-5. Comparison Between HM and HMD (M = Cr, Mo) Species

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<th>$\omega_{eH_e}^H$ (cm$^{-1}$)</th>
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<th>bond angle (°)</th>
<th>% anharmonicity</th>
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<td></td>
</tr>
<tr>
<td>H-CrD</td>
<td>1689.5</td>
<td>31.2</td>
<td>1.64</td>
<td>0.047</td>
<td>118 ± 5</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>H-Mo</td>
<td>1727.4</td>
<td>26.0</td>
<td>1.75</td>
<td>—</td>
<td>—</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>H-MoD</td>
<td>1776.8</td>
<td>28.4</td>
<td>1.86</td>
<td>0.042</td>
<td>110 ± 5</td>
<td>1.6</td>
<td></td>
</tr>
</tbody>
</table>

a. From reference 56.
can also be explained by the larger involvement of the 4d orbital in Mo. The calculated values for the stretching force constants, bond angles and the anharmonicities are listed in Table 3-5. There are several factors that make the bonding of second row transition metals different from that of first row transition metals. The radial overlap of the nd orbital with the (n+1)s orbital is larger for the second row than that of first row\(^{(52)}\). The 4d\(^n\)5s\(^2\) and 4d\(^{n+1}\)s\(^1\) configurations are also very close in energy which results in better s-d hybridization and greater d involvement in the bonds of second row transition metal hydrides. This is confirmed by the larger stretching force constant of MoH\(_2\) and the stronger Mo-H bonds.

The coupling force constants \((k_{12})\) for CrH\(_2\) and MoH\(_2\) are listed in Table 3-5 together with the stretching force constants.

3.5. SUMMARY

In summary, both Cr and Mo insert into the H-H bond to form MH\(_2\) upon photolysis with UV light, where MH\(_2\)(M = Cr and Mo) have been observed to be nonlinear molecules. Species such as CrH\(_3\), MoH, MoH\(_3\), MoH\(_4\), and MoH\(_6\) have also been detected as products from photolysis. The dimer of chromium has also been found to be isolated in Kr matrices and to react with H\(_2\).

The possible reactions observed in this study can be summarized as follows:
\[ M = \text{Cr, Mo} \]

\[ M + H_2 \xrightarrow{\text{UV (320 - 380 nm)}} \xrightarrow{12K} MH_2 \]

\[ M = \text{Cr, Mo} \]

\[ M + 2H_2 \xrightarrow{\text{UV (320 - 380 nm)}} \xrightarrow{12K} MH_3 + H \]

\[ M = \text{Cr} \]

\[ \text{CrH}_2(H_2) \xrightarrow{\lambda > 520 \text{ nm}} \xrightarrow{\text{UV (320 - 380 nm)}} \text{CrH}_3 + H \]

\[ \text{Cr}_2 + H_2 \xrightarrow{\lambda > 520 \text{ nm}} \xrightarrow{12K} \text{Cr}_2(t-H)_2 \]

\[ M = \text{Mo} \]

\[ \text{MoH}_2 + H_2 \xrightarrow{\lambda > 400 \text{ nm}} \xrightarrow{\text{UV (320 - 380 nm)}} \text{MoH}_4 \]

\[ \text{MoH}_4 + H_2 \xrightarrow{\lambda > 400 \text{ nm}} \text{MoH}_6 \]

\[ \text{Mo} + H^* \xrightarrow{12K} \text{MoH} \]

* where H atoms were produced over the hot Mo filaments
CHAPTER IV

PHOTOREACTIONS OF

CALCIUM AND ZINC WITH MOLECULAR HYDROGEN

4.1. INTRODUCTION

Ca and Zn are similar to one another in that they both have two valence electrons in the 4s orbital and both have a $^1S_0$ ground state. Ca, however, has empty 3d orbitals while Zn has fully occupied 3d orbitals. One expects that both Ca and Zn will tend to utilize their s and p orbitals in the formation of M-H bonds. An FT-IR matrix isolation study of reactions of Ca and Zn with H$_2$ can provide a good comparison of bonding changes of s, p and d orbitals from the beginning to the end of 3d transition metals. Additional information on the effects of empty versus full d orbitals can also be gained by comparison of the reaction behavior of Ca versus Zn.

The kinetic energy dependence of the reactions of ground-state Ca$^+$ and Zn$^+$ with molecular hydrogen and its isotopes has been examined using “guided” ion beam mass spectroscopy$^{(63)}$ by Armentrout et al. They observed that Ca$^+$ and Zn$^+$ fall into two distinct classes of reaction behavior due to their different electronic structure. The difference in the reactivity of Ca$^+$ and Zn$^+$ was explained by the different secondary interactions of the 3d$^n$ state of Ca and Zn with the $\sigma_u^*$ orbital of H$_2$. The dissociation energies for CaH$^+$ and ZnH$^+$ were found to be 1.97 ev and 2.36 ev, respectively.

Quantum mechanically Schilling et al$^{(64)}$ found that both CaH$^+$ and ZnH$^+$ have a $^1\Sigma^+$ ground state. The dissociation energies for CaH$^+$ and ZnH$^+$ were computed to be 2.03 ev and 2.39, respectively. Vibration
frequencies for CaH$^+$ and ZnH$^+$ were calculated to be 1467 cm$^{-1}$ and 1868 cm$^{-1}$. The relativistic and non-relativistic Hartree-Fock one-center expansion calculations for CaH$_2$ and ZnH$_2$ have been reported by Pyykkö$^{(65)}$. The calculated atomization energies (MH$_2$ → M + 2H) of CaH$_2$ and ZnH$_2$ are 2.07 ev and 1.48 ev, respectively.

Several studies of calcium hydrides have been carried out in recent years because of their astrophysical importance$^{(66)}$. The most recent experimental investigation was carried out by Petiprez et al$^{(67)}$ with infrared laser spectroscopy. The rotation-vibration bands of CaH and CaD were observed in the 10 μm region. Potential energy curves for the 13 first low lying electronic states of CaH have been recently calculated$^{(68)}$. The bond distance, $r_e$, and $\omega_e x_e$ for CaH in its ground state were calculated to be 2.10Å, 1253 cm$^{-1}$, and 20 cm$^{-1}$, respectively.

The neutral species of both CaH$^{(69)}$ and ZnH$^{(69)}$ have a $^2\Sigma^+$ ground state and measured vibrational frequencies of 1298.3 and 1607.6 cm$^{-1}$, respectively. Recently, the infrared spectra of CaH$^{(67)}$ and ZnH$^{(70)}$ with various isotopes have been extensively investigated using IR diode laser spectroscopy. The $\omega_e$'s for CaH and ZnH in their ground state were found to be 1298.77 cm$^{-1}$, and 1615.7 cm$^{-1}$, respectively.

Solid ZnH$_2$ was first made in 1977$^{(71)}$ by the following reaction in THF solutions:

$$(\text{CH}_3)_2\text{Zn} + \text{AlH}_3 \rightarrow \text{ZnH}_2 + (\text{CH}_3)_2\text{AlH}$$

However, little is known about molecular ZnH$_2$ since it is not stable at room temperature. Furthermore, the characterization of the Zn-H bonds is of
considerable interest with respect to understanding the mechanisms for the decomposition of diethylzinc (DEZn), \((\text{C}_2\text{H}_5)_2\text{Zn}\). This molecule is one of the major precursors\(^{(72)}\) used for CVD growth of Zn related semiconductor materials such as ZnS, ZnSe. ZnH\(_x\) has been detected\(^{(73)}\) directly as one of the fragments induced by UV light photolysis of diethylzinc.

In this study we have identified calcium dihydride and species containing dimers of calcium with terminal and bridging hydrogens in Xe and Kr matrices. The molecular dihydrogen complex \(\text{Ca}_2(\text{H}_2)_2\) has also been observed in Kr matrices. The stretching and bending frequencies have been identified for ZnH\(_2\) and Zn\(_2\)(t-H)\(_2\) in Ar and Kr matrices. The stretching force constants for CaH\(_2\) and ZnH\(_2\) are calculated to be 0.89 and 2.17 mdyn/Å, respectively.

4.2. EXPERIMENTAL

Refer to chapter I for experimental details. Briefly, Ca or Zn metal atoms are cotrapped with molecular hydrogen in an excess of the matrix gases (Ar, Kr, and Xe) on a rhodium coated copper surface over a period of 25 minutes. Calcium (99.9%, Alfa) and zinc (99.999%, Alfa) metals were vaporized through an approximately 2 mm diameter orifice from a stainless steel crucible enclosed in a resistively heated tantalum furnace. Ca and Zn were vaporized over the temperature ranges of 400 - 500 °C and 270 - 300 °C, respectively. The temperature was monitored by a Pt-Pt 13%Rh (0.005", Omega) thermocouple.
4.3. RESULTS

4.3.1. Zinc-Hydrogen

In a newly trapped Kr matrix containing atomic zinc and molecular hydrogen, no spontaneous reactions were evidenced. Only the previously reported\(^{74}\) water complex of zinc, Zn(H\(_2\)O), was seen upon deposition. The same matrix was then subject to irradiation with different energies. Photolysis with light of \(\lambda > 320\) nm caused no reactions. However, subsequent photolysis with UV (270 - 320 nm) light for 10 minutes on the same matrix yielded a peak at 1861.0 cm\(^{-1}\) and a strong peak at 625.3 cm\(^{-1}\) with a shoulder at 623.6 cm\(^{-1}\), as shown in Fig. 4-1. Fig. 4-1 also illustrates the IR spectra for reactions of Zn with D\(_2\), and HD in Kr matrices. All the spectra shown in Fig. 4-1 were recorded after 10-minute photolysis with UV (270 - 320 nm) light.

As seen in Fig.4-1(B), the peak at 1861.0 cm\(^{-1}\) in a H\(_2\) reaction shows a large shift to 1350.9 cm\(^{-1}\) when Zn reacts with D\(_2\). This strongly indicates that these bands are due to a M-H stretching mode. Due to detector limitations, the deuterium peak corresponding to 623.6 cm\(^{-1}\) in H\(_2\) reactions was not observed. Photolysis with UV (270 - 320 nm) light on a Kr matrix containing Zn and HD gave rise to a peak at 1861.0 cm\(^{-1}\) in the Zn-H stretching region which is also the same frequency observed in the H\(_2\) reactions, and a peak at 1340.0 cm\(^{-1}\) in the Zn-D stretching region. A peak at 548.9 cm\(^{-1}\) with a shoulder at 546.7 cm\(^{-1}\) was observed as well in the HD reactions which is thought to be the counter peak of 623.6 cm\(^{-1}\) observed in H\(_2\) reactions.
Because the peaks in the Zn-D stretching region occur at different frequencies for the D₂ and HD reactions, the possibility of assignment to zinc monohydrides, ZnH, is thus precluded. The spectral pattern leads to the assignment of the peaks at 1861.0 cm⁻¹ and at 1350.9 cm⁻¹ to the stretching frequencies of ZnH₂ and ZnD₂, respectively. We assigned the peaks at 625.3 and 548.9 cm⁻¹ to the bending frequencies for ZnH₂ and ZnHD, respectively. The bending frequency for ZnD₂ can be calculated approximately using the following equation for linear molecules:  

\[
\frac{\omega_2^i}{\omega_2} = \frac{\omega_3^i}{\omega_3} = \frac{m_y(1+\frac{2m_y^i}{m_{Zn}})}{m_y(1+\frac{2m_y}{m_{Zn}})}
\]

Where \(\omega_2, \omega_3, \text{ and } \omega_2^i, \omega_3^i\) are frequencies of bending and asymmetric stretching modes for ZnH₂, and ZnD₂, respectively, and \(m_y\) and \(m_y^i\) are the masses for H and D. The bending frequency for ZnD₂ is calculated to be 449.2 and 453.7 cm⁻¹ in a Kr and an Ar matrix respectively. The results are summarized in Table 4-1.

The peak at 1875 cm⁻¹ in a reaction with H₂ in Kr is thought to be due to a secondary matrix trapping site, since in the reaction with HD, the Zn-H and Zn-D stretchings are also accompanied by an adjacent weak feature. The shoulder on the bending mode is also a consequence of different matrix sites.

The reactions of Zn with H₂, D₂, and HD were also examined in Ar matrices. Fig. 4-2 displays a collection of IR spectra for the reaction products in Ar matrices after 10 minute photolysis with UV (270 - 320 nm)
Figure 4-1. Infrared spectra for the reactions of zinc with hydrogen in Kr matrices after 10 minutes photolysis with UV (270 - 320 nm) light.

(A) with H\textsubscript{2};
(B) with HD;
(C) with D\textsubscript{2};
(D) with a mixture of H\textsubscript{2} and D\textsubscript{2}.
Figure 4-2. Infrared spectra for the reactions of zinc with hydrogen in Ar matrices after 10 minutes photolysis with UV (270 - 320 nm) light.

(A) with H₂;
(B) with HD;
(C) with D₂.
light. In addition to the strong peaks which can be readily assigned to vibrations of zinc dihydride, Fig. 4-2(A) also exhibits a weak peak at 1850.1 cm\(^{-1}\) and two weak features at 600.8 and 612.5 cm\(^{-1}\) in a \(\text{H}_2\) reaction. In a reaction with HD, the above weak bands shifted to 1849.1 cm\(^{-1}\) in the Zn-H stretching region and 1331.9 cm\(^{-1}\) in Zn-D stretching region and two peaks at 529.4 and 537.5 cm\(^{-1}\) in the bending region. These bands are thought to result from a species relating to the dimer of zinc, \(\text{Zn}_2\). Since the stretching frequencies are in the terminal Zn-H region, a tentative assignment to \(\text{Zn}_2\text{H}_2\) with two terminal hydrogens is suggested. The observed frequencies and their assignments are also listed in Table 4-1. Because only one stretching mode was observed for \(\text{ZnH}_2\) in both Kr and Ar matrices, a linear geometry is assigned.
Table 4-1. The Observed Frequencies (cm$^{-1}$) for Zinc Hydrides

<table>
<thead>
<tr>
<th></th>
<th>ZnH$_2$</th>
<th>ZnD$_2$</th>
<th>ZnHD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kr</td>
<td>Ar</td>
<td>Kr</td>
</tr>
<tr>
<td>Zn-H stretching</td>
<td>1861.0</td>
<td>1870.8</td>
<td></td>
</tr>
<tr>
<td>Zn-D stretching</td>
<td></td>
<td></td>
<td>1350.9</td>
</tr>
<tr>
<td>bending</td>
<td>625.3</td>
<td>630.9</td>
<td>449.2$^a$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Zn$_2$H$_2$</th>
<th>Zn$_2$D$_2$</th>
<th>Zn$_2$HD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kr</td>
<td>Ar</td>
<td>Kr</td>
</tr>
<tr>
<td>Zn-H stretching</td>
<td>1850.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn-D stretching</td>
<td></td>
<td>1343.4</td>
<td></td>
</tr>
<tr>
<td>bending</td>
<td>600.8$^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>612.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. Calculated values using the harmonic stretching frequencies for ZnH$_2$
   and ZnD$_2$.

b denotes the stronger absorption.
4.3.2. Calcium-Hydrogen

Ca has been found to be mobile and dimerization of Ca in Kr and Ar matrices at 12 K is a well known fact. The absorption spectra of atomic Ca and the dimer of calcium, Ca$_2$, isolated in Ar, Kr and Xe have previously studied by Francies et al$^{76}$. They concluded that it is far easier to isolate atomic Ca in Xe than in Kr and Ar, and that essentially only calcium dimers can be isolated in an Ar matrix. The $^1S\rightarrow^1P$ and $^1S\rightarrow^1D$ atomic transitions for Ca were found to occur around 430 nm, 457 nm in Xe matrices and 420 nm, 454 nm in Kr matrices, respectively. Three strong absorption bands for Ca$_2$ have been observed at 480, 510, and 556 nm in a Kr matrix. In order to distinguish the atomic calcium reactions from reactions of calcium dimers, the reactions of Ca with hydrogen were studied in Xe and Kr matrices.

4.3.2.1. Reactions of Ca with H$_2$ in Xe

The IR spectra of the products from the photoreactions of Ca with H$_2$ in a Xe matrix are illustrated in Fig. 4-3. In a freshly trapped Xe matrix containing Ca and H$_2$, there was no evidence of spontaneous reactions, as seen in Fig. 4-3(A). Photolysis with light of $\lambda > 580$ nm for 10 minutes produced only a very weak peak at 1203 cm$^{-1}$ which can be readily assigned to the previously established molecule H-CaOH$^{77}$. Further photolysis with light of $\lambda > 450$ nm on the same matrix surface, however, created a new and strong peak at 1163.8 cm$^{-1}$. Subsequent photolysis with UV light caused no additional changes in the spectrum.
Figure 4-3. Infrared spectra for the reactions of calcium with H₂ in a Xe matrix.

(A) on a freshly trapped matrix;

(B) following 10 minutes photolysis with light of λ > 580 nm;

(C) following subsequent photolysis with light λ > 450 nm for 10 minutes.
Figure 4-4. Infrared spectra for the reactions of calcium with hydrogen in Xe matrices after 10 minutes photolysis with light of $\lambda > 450$ nm.

(A) with $\text{H}_2$;
(B) with $\text{HD}$;
(C) with $\text{D}_2$. 
The reactions of Ca with D₂ and HD were also investigated in Xe matrices. The resultant IR spectra recorded after 10 minutes photolysis with \( \lambda > 450 \) nm are summarized in Fig. 4-4. The above peak (1163.8 cm⁻¹) exhibits a large shift to 847.8 cm⁻¹ in the reactions with D₂. These two peaks underwent small shifts in the HD reactions to 1201.7 and 864.0 cm⁻¹ in the Ca-H and Ca-D stretching regions, respectively. These results are similar to those obtained for the reactions of Zn with molecular hydrogen described above. For the same reasons, we assign the peak at 1163.8 cm⁻¹ as the asymmetric stretch for CaH₂ and 847.8 cm⁻¹ as the asymmetric stretch for CaD₂. The observed frequencies for calcium dihydride, CaH₂, are summarized in Table 4-2. The bending frequency has not been determined experimentally. However, it was computed(78) recently to be 157 cm⁻¹. The harmonic frequencies (\( \omega_0 \)) for CaH₂ were calculated to be 1336, and 1257 cm⁻¹ for symmetric and antisymmetric stretches, which is consistent with our measured values, allowing for the matrix perturbations.

4.3.2.2. Reactions of Ca with H₂ in Kr

Fig. 4-5 depicts the IR spectra from reactions and photolysis of a Kr matrix containing calcium and molecular hydrogen. The spectrum of a freshly trapped Kr matrix indicates that no reactions occur spontaneously as in a Xe matrix. In the spectrum recorded after 10 minute photolysis with light of \( \lambda > 580 \) nm, a group of intense peaks centered at 1237.6 cm⁻¹ (peak a), and several weak peaks at 1044.5 cm⁻¹ (peak b), 970.7 cm⁻¹ (peak c), and 869.3 cm⁻¹ (peak d) were observed. Further photolysis with light of
Table 4.2. The Observed Frequencies (cm\(^{-1}\)) for Calcium Dihydride

<table>
<thead>
<tr>
<th></th>
<th>CaH(_2)</th>
<th>CaD(_2)</th>
<th>CaHD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kr</td>
<td>Xe</td>
<td>Kr</td>
</tr>
<tr>
<td>asym stretching</td>
<td>1192.0</td>
<td>1163.8</td>
<td>866.8</td>
</tr>
<tr>
<td></td>
<td>(1.171)*</td>
<td>(0.922)</td>
<td></td>
</tr>
<tr>
<td>sym stretching</td>
<td>1267.0</td>
<td>1239.8</td>
<td>899.1</td>
</tr>
<tr>
<td></td>
<td>(0.014)</td>
<td>(0.012)</td>
<td></td>
</tr>
</tbody>
</table>

* The numbers in parentheses provide a relative measurement of the intensities of the two stretching modes.
Figure 4-5. A collection of IR spectra for photoreactions of calcium with H$_2$ in a Kr matrix.

(A) a freshly trapped matrix;

(B) following 10 minutes photolysis with light of $\lambda > 580$ nm;

(C) following subsequent photolysis with light of $\lambda > 520$ nm for 10 minutes;

(D) following 10 minutes photolysis with UV (320 - 380 nm) light.

\[ a = \text{Ca}_2(t\text{-H})_2; \quad b = \text{Ca}_2(H_2)_2; \quad c = \text{Ca}_3(t\text{-H})_2; \quad d = \text{Ca}_2(t\text{-H})_2(b\text{-H})_2; \quad e = \text{CaH}_2. \]
\( \lambda > 520 \) nm for 10 minutes on the same matrix surface increased the intensities for peaks \( b, c, d \) dramatically and meanwhile weakened peak \( a \) significantly. Due to the fact that all the above peaks were produced by irradiation with \( \lambda > 520 \) nm light (as mentioned above atomic Ca does not have optical transitions in this region) and that they were not present in Xe matrices, we concluded that they are due to clusters of calcium (such as Ca\(_2\), Ca\(_3\)) related species. Subsequent exposure of the matrix surface to UV (320 - 380 nm) light on the other hand yielded a new peak at 1196.4 cm\(^{-1}\) (labeled \( e \)) and intensified the peaks \( c \) and \( d \). UV photolysis further decreased the intensity for peak \( a \). It was also noticed that photolysis with UV light weakened band \( b \), and prolonged photolysis with UV (320 - 380 nm) removed peak \( a \) and further increased peak \( e \).

In order to identify the above peaks, extensive studies on Ca and H\(_2\) concentrations have been carried out in Kr matrices. The resultant IR spectra for a series of reactions with a constant H\(_2\) pressure and different Ca concentrations from are collected in Fig. 4-6. It is verified that only group \( e \) seems to involve one Ca atom and that groups \( a, b, \) and \( d \) are the dimer, Ca\(_2\), related species. The slight decrease in intensity for band \( e \) at the highest Ca concentration suggests that at a high concentration of Ca, atomic Ca becomes saturated, and the dimer of Ca becomes the dominant reactive species.

Fig. 4-7 is a summary of the IR spectra for a series of studies with a constant Ca concentration and varying amounts of H\(_2\). Group \( c \) appears to involve only one H\(_2\) molecule. It is also noticed from Fig. 4-6 that group \( c \) appears to increase more rapidly at high calcium concentrations than the other peaks (\( a, b, \) and \( d \)). We suggest that group \( c \) results from a reaction of
Figure 4-6. A summary of IR spectra for the photoreactions of constant $\text{H}_2$ pressure with different Ca concentrations in Kr matrices.

(I) after 10 minutes photolysis with $\lambda > 580$ nm;

(II) after 10 minutes photolysis with $\lambda > 520$ nm;

(III) after subsequent photolysis with UV (320 - 380 nm) light,

where the temperatures for vaporizing Ca are:

(A) 412° C;

(B) 430° C;

(C) 453° C;

(D) 476° C;

(E) 495° C;

(F) 515° C.
Figure 4-7. A summary of IR spectra for the photoreactions of constant Ca concentration with different H₂ pressures in Kr matrices.

(I) after 10 minutes photolysis with \( \lambda > 580 \) nm;

(II) after 10 minutes photolysis with \( \lambda > 520 \) nm;

(III) after subsequent photolysis with UV (320 - 380 nm) light,

where the pressures for H₂ are:

(A) \( 3.0 \times 10^{-7} \) Torr;

(B) \( 5.5 \times 10^{-7} \) Torr;

(C) \( 8.0 \times 10^{-7} \) Torr;

(D) \( 1.0 \times 10^{-6} \) Torr;

(E) \( 2.0 \times 10^{-6} \) Torr;
the trimer of calcium, Ca$_3$. Ca$_3$H$_2$ is thus assigned to group c with two terminal hydrogens. The geometry (linear, bent, or triangle) for this molecule can not be determined with the limited information.

It is also seen from the H$_2$ and Ca concentration studies that band e includes one Ca atom and one H$_2$ molecule. By comparison with the reactions in Xe matrices, we assign band e to calcium dihydride, CaH$_2$. Band e appears to include two peaks at 1196.4 and 1193.0 cm$^{-1}$, and it is noted in Fig. 4-7 that the peak at 1193.0 cm$^{-1}$ appears to involve two H$_2$ molecules and we suggest that this peak is due to a weak complex of CaH$_2$ with a second H$_2$ molecule, CaH$_2$(H$_2$). No such splitting was seen in D$_2$ and HD reactions.

Fig. 4-8 illustrates the IR spectra for photoreactions of Ca with D$_2$ in a Kr matrix. Bands a and b shifted to 892.2 and 761.5 cm$^{-1}$, respectively. Group c (Ca$_3$D$_2$) was observed at 789.9 and 707.7 cm$^{-1}$. CaD$_2$ (band e) has a stretching frequency at 866.4 cm$^{-1}$. Group d includes peaks at 813.1, 738.6 and 628.2 cm$^{-1}$. The corresponding peak to 599.0 cm$^{-1}$ in a H$_2$ reaction was not observed due to the lower limit of the spectrometer. The weak peak at 566.9 cm$^{-1}$ is thought to be the bending frequency for HCaOH(77).

The reactions of Ca with HD in a Kr matrix have also carried out and the IR spectra are summarized in Fig. 4-9. The analogues peaks to band a were found to be at 1245.4 and 897.7 cm$^{-1}$ for the Ca-H and Ca-D stretches, respectively. As seen in Fig. 4-9(B), photolysis with light of $\lambda > 520$ nm, which usually produces band b, generates a peak at 881.8 cm$^{-1}$. This peak can not be assigned to the stretch for CaHD since no corresponding band was observed in the Ca-H stretch region. It was concluded earlier from concentration studies that peak b is contributed by a species which includes
Figure 4-8. A collection of IR spectra for the photoreactions of calcium with D$_2$ in a Kr matrix.

(A) a freshly trapped matrix;
(B) following 10 minutes photolysis with light of $\lambda > 580$ nm;
(C) following 10 minutes subsequent photolysis with light of $\lambda > 520$ nm;
(D) following 10 minutes photolysis with UV (320 - 380 nm) light.

a = Ca$_2$(t-D)$_2$; b = Ca$_2$(D)$_2$; c = Ca$_3$(t-D)$_2$; d = Ca$_2$(t-D)$_2$(b-D)$_2$; e = CaD$_2$. 
Fig. 4-9. A collection of IR spectra for the photoreactions of calcium with HD in a Kr matrix.

(A) a freshly trapped matrix;
(B) following 10 minutes photolysis with light of $\lambda > 580$ nm;
(C) following 10 minutes subsequent photolysis with light of $\lambda > 520$ nm;
(D) following 10 minutes photolysis with UV (320 - 380 nm) light.

\[ a = \text{Ca}_2(\text{t-HD}); \quad b = \text{Ca}_2(\text{HD})_2; \quad c = \text{Ca}_3(\text{t-HD}); \quad d = \text{Ca}_2(\text{t-HD})(\text{b-HD}); \quad e = \text{CaHD} \]
two Ca atoms and more than one H₂ molecule. As indicated in Fig. 4-8, band b shifted to 762.5 cm⁻¹ in a reaction with D₂. The peak at 881.8 cm⁻¹ in reactions with HD is seen to lie in the near middle of corresponding b peaks in H₂ and D₂ reactions. This strongly suggests that band b is due to a molecular complex species. As noticed in the Ca concentration studies band b is due to a Ca₂ related species, and we tentatively assign this feature to Ca₂(H₂)₂. The H-H vibrational mode of this complex is expected to absorb at much higher frequencies, i.e. ~3000 cm⁻¹, and to exhibit a characteristically very low intensity. The dihydrogen complexes for atomic Pd(79), Ni(80), and small clusters of Fe(81) and Cu(81) were reported previously. However, the Ca₂(H₂)₂, represents the first example for a main group metal cluster.

Peak a which results from species containing Ca₂ and one H₂ molecule, and exhibits terminal Ca-H stretching frequencies, is tentatively assigned to:

\[
\text{H} - \text{Ca} - \text{Ca} - \text{H}
\]

As seen in Table 4-3, the corresponding Ca₂HD species has frequencies much closer to those for Ca₂H₂ and Ca₂D₂ than is the case for CaH₂ and CaD₂. The increased separation of the two Ca-H bonds in the above structure is consistent with this smaller interaction.

Band d is thought to be related to the dimer, Ca₂, and two hydrogen molecules, since the band d peaks found in a reaction with HD were also present in a reaction with a mixture of H₂ and D₂. Two peaks in H₂ reactions (1124.3 and 1024.3 cm⁻¹) are thought to be terminal Ca-H
stretching modes and two peaks at 869.7 and 596.6 cm\(^{-1}\) are assigned to bridging Ca-H stretching modes. A molecule with both terminal and bridging hydrogens with the following structure is tentatively suggested:

![Chemical structure](image)

The observed frequencies for the above species in Kr matrices are listed in Table 4-3.

Fig. 4-10 illustrates the IR spectra for reactions of Ca with H\(_2\), HD, and D\(_2\) in Kr matrices after consecutive photolyses with light of \(\lambda > 580\) nm, \(\lambda > 450\) nm, and UV (320 - 380 nm). The stretching frequencies for CaHD were observed at 1228.4 and 882.3 cm\(^{-1}\). As illustrated in Fig. 4-10, very weak peaks at 1267.0 cm\(^{-1}\) in the H\(_2\) reaction and at 900 cm\(^{-1}\) in the D\(_2\) reaction are also present. Similar weak features are also seen in Xe matrices at 1239.8 and 885.2 cm\(^{-1}\) for H\(_2\) and D\(_2\) reactions, respectively. Since there are no analogous weak peaks in the HD reaction, we tentatively assigned these weak features to the symmetric stretching frequency for calcium dihydride. The observation of a very weak symmetric stretching mode for CaH\(_2\) in Kr and Xe indicates that CaH\(_2\) is a slightly bent molecule in both Xe and Kr matrices which suggests that calcium utilizes some of its 3d orbitals in bonding with hydrogen. An approximate bond angle for CaH\(_2\) can be obtained from the relative peak intensities of the weak symmetric mode and antisymmetric mode. The bond angle is 168° calculated from the integrated
Fig. 4-10. Infrared spectra for reactions of calcium with hydrogen in Kr matrices after consecutive photolyses with $\lambda > 580$ nm, $\lambda > 520$ nm and UV (320 - 380 nm) light.

(A) with $\text{H}_2$;
(B) with HD;
(C) with $\text{D}_2$. 
Table 4-3. Reaction Product Absorptions (cm\(^{-1}\)) for Reactions of Ca with H\(_2\) in Kr Matrices.

<table>
<thead>
<tr>
<th>obs. frequencies (cm(^{-1}))</th>
<th>assignments</th>
<th>label</th>
</tr>
</thead>
<tbody>
<tr>
<td>1561.3</td>
<td>Ca(H(_2)O)</td>
<td></td>
</tr>
<tr>
<td>1246.3, 898.2</td>
<td>Ca(_2)(t-HD)</td>
<td>a</td>
</tr>
<tr>
<td>1237.4</td>
<td>Ca(_2)(t-H(_2))</td>
<td>a</td>
</tr>
<tr>
<td>1228.4, 882.5</td>
<td>CaHD</td>
<td>e</td>
</tr>
<tr>
<td>1205.3</td>
<td>HCaOH</td>
<td></td>
</tr>
<tr>
<td>1267.0, 1192.0</td>
<td>CaH(_2)</td>
<td>e</td>
</tr>
<tr>
<td>1124.3, 1024.3, 869.7, 596.6</td>
<td>Ca(_2)(t-H(_2))(b-H(_2))</td>
<td>d</td>
</tr>
<tr>
<td>1099.7, 970.7</td>
<td>Ca(_3)H(_2)</td>
<td>c</td>
</tr>
<tr>
<td>1057.5, 764.0, 869.2, 643.9</td>
<td>Ca(_2)(t-HD)(b-HD)</td>
<td>d</td>
</tr>
<tr>
<td>1044.3</td>
<td>Ca(_2)(H(_2))(_2)*</td>
<td>b</td>
</tr>
<tr>
<td>1005.0, 720.0</td>
<td>Ca(_3)HD</td>
<td>c</td>
</tr>
<tr>
<td>892.2</td>
<td>Ca(_2)(t-D(_2))</td>
<td>a</td>
</tr>
<tr>
<td>881.8</td>
<td>Ca(_2)(HD(_2))(_2)*</td>
<td>b</td>
</tr>
<tr>
<td>899.1, 866.4</td>
<td>CaD(_2)</td>
<td>e</td>
</tr>
<tr>
<td>813.1, 738.6, 628.2</td>
<td>Ca(_2)(D(_2))(_2)(_2)</td>
<td>d</td>
</tr>
<tr>
<td>789.9, 707.7</td>
<td>Ca(_3)D(_2)</td>
<td>c</td>
</tr>
<tr>
<td>761.5</td>
<td>Ca(_2)(D(_2))(_2)*</td>
<td>b</td>
</tr>
</tbody>
</table>

* indicates that the hydrogens are molecularly complexed to the dimer of calcium, Ca\(_2\).
intensities which are listed in Table 4-2. If the measured ratio is assumed to be a factor of two greater or less, the calculated angles are 172° and 164°, respectively. The closely related molecule CaF₂ has also been found to be bent, where the bond angle has been measured\(^{(82)}\) to be 140°.

However, for atomic Zn, the 3d orbitals are much lower in energy and actually lie lower than the \(\sigma_g\) orbital of H₂. Thus, the 3d electrons of Zn are really core electrons and should have minimal interactions with the orbitals of H₂. On the other hand, the 4d orbitals are so high in energy that the promotion from 4s to 4d requires an energy as high as 62458 cm\(^{-1}\). Only one stretching mode has been identified for both ZnH₂ and ZnD₂, and a linear geometry is assigned to zinc dihydride, as expected from orbital consideration. The related family, ZnF₂\(^{(83)}\) has also been determined as a linear molecule. It has been found that excitation of the \(^3\!P_1\) atomic Zn\(^{(84)}\), through the \(^1\!S_0 \rightarrow ^3\!P_1\) transition causes the reaction with H₂. We thus conclude that the \(^1\!S_0\) ground state is unreactive towards insertion into the H-H bond while the \(^3\!P_1\) or lower energy excited states to which it decays is a reactive state which leads to insertion into the H-H bond to form ZnH₂. Zinc largely utilizes its s, p orbitals to form Zn-H bonds and linear ZnH₂. It is unlike other earlier transition metals where the M-H bonds have appreciable amounts of d character.

4.4. DISCUSSION

Both atomic Ca and Zn do not react with molecular hydrogen in their ground states. This can be understood by simple MO considerations. Both Ca and Zn have a filled 4s\(^2\) valence orbital. When the metals interact with
molecular hydrogen in a $C_{2v}$ symmetry, the 4s orbital of the metal centers and the $\sigma_g$ orbitals of $H_2$ combine to form a bonding molecular orbital and an antibonding molecular orbital. Since the $\sigma_g$ orbital of $H_2$ is fully occupied, the occupation with two electrons in the 4s orbital will lead to double occupation of the antibonding MOs, with no direct bonding. Thus for Ca and Zn to react with $H_2$, one 4s electron must be promoted to a higher p or d orbital. Selection rule allowed transitions for atomic calcium are $^1S \rightarrow ^1P$ (23652 cm$^{-1}$) and $^1S \rightarrow ^1D$ (21850 cm$^{-1}$). It is observed that excitation at these wavelengths does lead to metal insertion into the $H_2$ bond to form the dihydride.

We know that the interaction of a metal with $H_2$ occurs primarily through two orbital pathways. On the one hand the $\sigma_{H_2}$ orbital can overlap with $\sigma$ orbitals of the metal; on the other hand orbitals of the metal with the same symmetry as the antibonding orbital of $H_2$ can back donate electrons to the $\sigma_{H_2}^*$ orbital. Ca has empty 4p and 3d orbitals and can use both sp or sd hybrids to form CaH$_2$. It is apparent that excitation of the atom from s to p or d orbitals allows simultaneous donation into the antibonding orbital of $H_2$ while also allowing electron donation from the $H_2$ $\sigma$ orbital to the metal 4s orbital.

The stretching force constants for dihydrides of Ca and Zn were obtained with a diatomic approximation using frequencies for the HMD species, provided the the vibrational coupling between M-H and M-D stretchings is small. The stretching force constants of CaH$_2$ and ZnH$_2$ are calculated to be 0.89 and 2.17 mdyn/Å, respectively. The force constants for CaH and ZnH were also calculated using frequencies from reference 69. These values for MH and MHD species are listed in Table 4-4. The difference in
the stretching force constants for CaH₂ and ZnH₂ may result from two clear differences between Ca and Zn. One is the atomic radius, Ca has a covalent radius of 1.74 Å while the covalent radius for Zn is 1.25 Å. ZnH₂ will have a much shorter bond length than that of CaH₂ and thus a larger force constant. The other factor is the electronegativity differences between Ca and Zn with Zn being more electronegative. Thus CaH₂ is expected to posses more ionic bonding character than ZnH₂ which will effectively lower the force constant due to longer range of electromagnetic force. As shown in Table 4-4 the force constant of ZnH is much lower than that for ZnH₂ while that for CaH is slightly higher than that of CaH₂. The much smaller force constant for ZnH is apparently reflecting the large s-p promotion energy which must be paid to form the initial bond. In ZnH₂ this promotion energy can be shared by two Zn-H bonds. The promotion energy requirements for Ca are much smaller which is also reflected in only a small difference between the force constants of CaH and CaH₂.

The coupling between the two M-H stretchings in MH₂ is represented by the force constants k₁₂(MH₂). As mentioned above, only the antisymmetric stretching was definitely assigned to ZnH₂. However, if one makes an assumption that the stretching frequencies of MHD occur at the middle of the two stretching modes of MH₂ and MD₂, one can deduce the symmetric stretching frequency for ZnH₂. The resultant k₁(MH₂) is 2.17 mdyn/Å for ZnH₂, which is consistent with the result obtained through a diatomic approximation. If one takes the assigned antisymmetric mode for CaH₂ and the tentatively assigned symmetric mode, one obtains a value of 0.89 mdyn/Å. The assigned symmetric mode is also consistent with the recent
Table 4-4. Comparisons Between MH and MHD (M = Ca, Zn) Species

<table>
<thead>
<tr>
<th></th>
<th>$\omega_e H$ (cm$^{-1}$)</th>
<th>$\omega_e H_X H$ (cm$^{-1}$)</th>
<th>$k_{M-H}$ (mdyn/Å)</th>
<th>$k_{12(MH_2)}$ (mdyn/Å)</th>
<th>bond angle ($^\circ$)</th>
<th>% anharmonicity</th>
<th>$\omega_e H_X H / \omega_e H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Ca$^a$</td>
<td>1298.3</td>
<td>19.1</td>
<td>0.98</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.5</td>
</tr>
<tr>
<td>H-CaD</td>
<td>1240.8</td>
<td>6.2</td>
<td>0.89</td>
<td>0.07</td>
<td>168 ± 5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>H-Zn$^a$</td>
<td>1607.6</td>
<td>55.1</td>
<td>1.51</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>3.4</td>
</tr>
<tr>
<td>H-ZnD</td>
<td>1927.4</td>
<td>33.2</td>
<td>2.17</td>
<td>0.03</td>
<td>~180</td>
<td>1.7</td>
<td></td>
</tr>
</tbody>
</table>

a. From reference 69.
calculated value. The respective derived $k_{12}$ values for CaH$_2$ and ZnH$_2$ are listed in Table 4-4 together with the stretching force constants.

4.5. SUMMARY

We have found in this study that excited atomic Ca and Zn react with molecular hydrogen at $\sim$12K to form MH$_2$ ($M =$ Ca, Zn), where CaH$_2$ probably has a slightly nonlinear geometry while ZnH$_2$ is a linear molecule. In Kr matrices, the ligand free dihydrogen complex Ca$_2$(H$_2$)$_2$ has also been identified as a product of photolysis with light $\lambda > 520$ nm. Excitation of diatomic and triatomic (Ca$_2$, Ca$_3$) has been found to facilitate insertion into the H-H bond to form species with terminal and/or bridging hydrogens.

The observed reactions can be summarized as follows:
\[ M = \text{Ca, Zn} \]

\[ \begin{align*}
M + H_2 & \xrightarrow{\text{hv}} MH_2 \\
M_2 + H_2 & \xrightarrow{\text{hv}} M_2(t-H)_2 \\
\end{align*} \]

\[ M = \text{Ca} \]

\[ \begin{align*}
\text{Ca}_2 + 2H_2 & \xrightarrow{\text{UV(320-380nm)}} \text{Ca}_2(t-H)_2(b-H)_2 \\
\text{Ca}_3 + H_2 & \xrightarrow{\text{UV(320-380nm)}} \text{Ca}_3(t-H)_2 \\
\text{Ca}_2 + 2H_2 & \xrightarrow{\lambda > 520 \text{ nm}} \text{Ca}_2(H_2)^* \_2 \\
\end{align*} \]

* where \( H_2 \) is molecularly coordinated to \( \text{Ca}_2 \).
CHAPTER V

REACTIONS OF
GALLIUM AND GERMANIUM WITH HYDROGEN AND METHANE

5.1. INTRODUCTION

Gallium hydrides have been actively studied throughout last several decades. The vapor-phase transients GaH\(^{(85)}\) and GaH\(_{3}\)\(^{(86)}\) were first reported in early 1960's. Lately, the infrared spectra of isotopic species of gallium hydride, \(^{69}\)GaH\(^{(87)}\), \(^{71}\)GaH\(^{(87)}\), and GaD\(^{(88)}\) were extensively reinvestigated by Jones et al using a diode laser spectrometer. The recent success\(^{(89, 90)}\) in synthesis and characterization of digallane (Ga\(_2\)H\(_6\)) by Downs, Goode, and Pulham is of great importance, since little is known about the structural properties and the stability of this molecule. The electronic diffraction study has shown that Ga\(_2\)H\(_6\) has a similar structure as B\(_2\)H\(_6\). Stimulated by the report, several theoretical studies on the properties of a variety of gallium hydrides have been conducted. Ga\(_2\)H\(_4\) was studied theoretically by Lammertsma and Leszcynski\(^{(91)}\), and they concluded that Ga\(_2\)H\(_4\) has an ionic structure Ga\(^+\)(GaH\(_4\))\(^-\) in its ground state with several isomers close in energies. Digallane, Ga\(_2\)H\(_6\),\(^{(92)}\) and trigallane (Ga\(_3\)H\(_9\))\(^{(93)}\) were studied by Schaefer et al. The equilibrium molecular structure and the infrared frequencies for all the vibrational modes have been reported. It was found that Ga\(_3\)H\(_9\) has a six member ring structure (Ga\(_3\)(b-H)\(_3\)(t-H)\(_6\)).
Because of their tremendous importance in semiconductor industry, the growth of gallium related compounds such as GaAs, GaAsAl etc, has been extensively investigated. Trimethyl gallium (TMG)\(^{94}\) is a widely used precursor in CVD processes. Aiming at understanding the mechanism of the CVD reactions, much attention\(^{95}\) has been given to understanding the process of decomposition of Ga(CH\(_3\))\(_3\) under different conditions. The bond energies for the first, second and third Ga-CH\(_3\) bonds in TMG\(^{96}\) were found to be ~61, ~35, and ~76 kcal/mol, respectively. Ga(CH\(_3\)) radical has been directly detected by Stuke et al\(^{97}\) using the far UV laser mass spectrometer as a UV laser fragment from gaseous TMG. Recently, a novel compound\(^{98}\) (t-Bu)\(_2\)Ga-As(t-Bu)\(_2\) has been synthesized as a single precursor for GaAs growth, and a β-elimination scheme was proposed as one of the decomposition mechanisms, in which a H-Ga bond was formed. A similar mechanism was also proposed for decomposition for Ga(C\(_2\)H\(_5\))\(_3\)\(^{99}\). The general interest in gallium chemistry suggests that characterization of both Ga-H and Ga-C bonds by matrix isolation infrared spectroscopy is of interest both experimentally and theoretically.

Research on small clusters of main group and transition metals has been an active area. The dimer of gallium, Ga\(_2\), was first studied by Ginter\(^{100}\) and later by Douglas et al\(^{101}\). Recently Balasubramanian investigated the dimer and trimer of gallium theoretically\(^{102}\). The Ga\(_2\) molecule has been found to have a \(^3\)\(\Pi_u\) electronic ground state. The dissociation energy of Ga\(_2\) was determined to be 110.3 KJ/mol by Shim et al\(^{103}\). Balasubramanian et al\(^{102}\) also computed the spectroscopic properties and potential energy surfaces of the trimer of gallium, Ga\(_3\). They concluded that the ground state of Ga\(_3\) is a \(^2\)\(A_1\) state with a
equilibrium geometry of a near-equilateral triangle with two very low-lying excited electronic states \( ^4A_2 \), and \( ^2B_1 \). However, no experimental spectroscopic data on these clusters and no information about the reactivities of these clusters have been reported. It is possible that the reactions of the \( \text{Ga}_2 \) and \( \text{Ga}_3 \) with molecular hydrogen and methane will provide useful information with regard to the absorption of \( \text{H}_2 \) and \( \text{CH}_4 \) on GaAs surfaces and to the understanding mechanisms of the growth of Ga related species using the CVD process.

Laser induced fluorescence (LIF) \(^{(104)}\) from \( ^2\text{S} \leftrightarrow ^2\text{P} \) transition of gaseous Ga atoms has recently been found to be very efficiently quenched by methane and no effect by \( \text{H}_2 \) could be detected under the experimental conditions used. The activation of \( \text{CH}_4 \) with photoexcited transition metal atoms has been extensively studied\(^{(105)}\). Recently, Ault et al\(^{(106)}\) have also studied the adduct of \( \text{Ga}(\text{CH}_3)_3: \text{AsH}_3 \).

This study focuses on the syntheses and characterization of the hydrides for atoms, dimers, and trimers of gallium and germanium using matrix isolation FT-IR spectroscopy, as part of our efforts on the reactivity of transition and main group metals with \( \text{H}_2 \) and \( \text{CH}_4 \). Vibrational frequencies for \( \text{GeH}_4 \), \( \text{GeH}_2 \) and species due to the dimer of germanium have been identified. Both \( \text{GaH}_2 \) and \( \text{GeH}_2 \) are bent molecules.

5.2. EXPERIMENTAL

Refer to Chapter I for experimental details. Gallium metal (Alfa Products, 99.99%) was placed in an alumina crucible enclosed in a resistively heated tantalum furnace and vaporized in the temperature
range of 900 - 1100°C. Germanium metal (Alfa Products, 99.9999%) was obtained from a graphite cell over the temperature range of 1200 - 1400 °C. The temperatures were measured with an optical pyrometer.

Reactant gases CH₄ (99.97%, Matheson), ¹³CH₄ (99.3% atom¹³C, Isotec, Inc.), and CD₄ (99% atom D, U.S. services, Inc.) were used as purchased.

5.3. RESULTS

5.3.1. Reactions of Gallium with Hydrogen

Fig. 5-1 displays the IR spectra of a matrix containing Ga and H₂ in an excess of Ar, where the ratio of Ga : Ar is ~ 15 : 1000 (The temperature of the furnace was at 1100°C). Six distinct sets of peaks labeled as a - e in Fig. 5-1 have been observed upon cocondensation and photolyses with light of different energies. It is noticed that the IR spectrum of a freshly trapped matrix includes several intense peaks around 1000 cm⁻¹ (band a) and few weak features between 1900 and 1500 cm⁻¹. The exposure of the matrix surface to light of λ > 520 nm did not cause any significant changes in the spectrum. Further photolysis with the light of 400 nm < λ < 520 nm, however, considerably decreased the intensity of band a and enhanced the growth of band b (with peaks at 1765.0, 1752.7 and 752.1, 746.8 cm⁻¹) and band c (with peaks at 1686.2 and 725.1 cm⁻¹). Subsequent irradiation with UV (320 - 380 nm) light on the same matrix diminished bands b and c and gave rise to band a again as seen in Fig. 5-1(C). Meanwhile, peaks d (including two peaks at 1799.0 and 1727.9 cm⁻¹) and e (one peak at 1514.1 cm⁻¹) were seen to increase in intensities. The intensities of bands d and e were dramatically increased after exposure to light of 280 - 320 nm, as seen
Figure 5-1. Infrared spectra for a matrix with Ga and H\textsubscript{2} in an excess of Ar.

(A) on deposition;
(B) following photolysis with light of 450 - 520 nm for 10 minutes;
(C) following subsequent photolysis of 320 - 380 nm for 10 minutes;
(D) following subsequent photolysis of 270 - 320 nm for 10 minutes.

\textbf{a} = \text{Ga}_2(\text{b-H})_2; \textbf{b} = \text{Ga}_3(\text{t-H})_2; \textbf{c} = \text{Ga}_2(\text{t-H})_2; \textbf{d} = \text{GaH}_2; \textbf{e} = \text{GaH},

where \textbf{b} and \textbf{t} represent bridging and terminal hydrogens.
Figure 5-2. A summary of IR spectra for the reactions of gallium with hydrogen in Ar matrices, after photolysis with UV (270 - 380 nm) light.

(A) with H$_2$;
(B) with HD;
(C) with D$_2$. 
Fig. 5-3. Same as Fig. 5-2. Spectra were recorded after subsequent photolysis of λ > 450 nm for 10 minutes on the respective matrices. The absorbance unit is the same as in Fig. 5-2.
in Fig. 5-1 (D).

All the bands mentioned above showed a large isotopic shift when D₂ was employed, as illustrated in Fig. 5-2 and Fig. 5-3, which strongly indicates that all bands are due to Ga-H vibrations. Fig. 5-2 is a collection of IR spectra for reactions of gallium with H₂, HD, and D₂ after the respective matrices were photolyzed with UV (280 - 370 nm) light. As noticed in Fig. 5-2(B), in the reactions of Ga with HD, the spectrum was complicated by the coexistence of Ga-H and Ga-D vibrations. Nevertheless, band e also appears in this spectrum at 1514.1 cm⁻¹ in the Ga-H stretching region and at 1090.3 cm⁻¹ in the Ga-D stretching region which are also present at these precise frequencies in the reactions with H₂ and D₂, respectively. From the Ga concentration studies described later, we conclude that only one Ga atom is involved in this molecule, and we assign this(band e) as gallium monohydride, GaH. The vibrational frequency of GaH in the gas phase(69) was observed to be at 1546.9 cm⁻¹ (ω = ωₑ - 2ωₑXₑ) which suggests that GaH has a moderate gas-matrix shift of ~ 37 cm⁻¹.

The IR spectra from a series of studies in which the amount of added H₂ was kept constant and the concentration of Ga was increased gradually (where the temperature of the furnace was increased from 900 to 1100°C) are shown in Figures 5-4 and 5-5, where the matrices were irradiated with UV and 400 - 500 nm light (after UV photolysis), respectively. As seen in Fig. 5-4 and 5-5, it is clear that as the concentration of Ga increases, the intensities of bands d and e (GaH) arise steadily, which strongly suggests that bands d and e do indeed result from atomic gallium species. The absorption bands a, b, and c seem to be predominantly present under higher gallium concentrations. The Ln-Ln plots(107) of the intensities of
Figure 5-4. A collection of IR spectra for a series of reactions with different gallium concentrations in Ar matrices (while the pressure of H₂ was kept the same). The spectra were taken after photolysis with UV (270 - 380 nm) light. The temperatures of vaporization for Ga were:

(A) 890°C;
(B) 947°C;
(C) 980°C;
(D) 1030°C;
(E) 1060°C;
(F) 1100°C.
Fig. 5-5. Same as Fig. 5-4. All spectra were recorded after subsequent photolysis of $\lambda > 450$ nm for 10 minutes on the respective matrices.
Figure 5-6. Plot of Ln[A(x)] versus Ln[A(GaH)]. A(x) is the absorbance of band x.

\[ a = \text{Ga}_2(b-H)_2; \quad b = \text{Ga}_3(t-H)_2; \quad c = \text{Ga}_2(t-H)_2; \quad d = \text{GaH}_2; \quad e = \text{GaH}. \]

The slopes of lines a, b, c, and d are 2.2, 2.9, 2.2, and 1.1(v_1), 1.0(v_3), respectively.
bands corresponding to each species versus the absorption of GaH is shown in Fig. 5-6, where the intensity of GaH is used as the internal standard to measure the number of gallium atoms present in species responsible for the other bands. It is suggested from the slopes of the lines that the absorption band d (two peaks with slopes of 1.1 and 1.0) corresponds to atomic Ga reactions and both bands a and c (with slopes of 2.2 and 2.2, respectively) are due to diatomic Ga$_2$ reactions, while band b (with a slope of 2.9) may arise from a triatomic Ga$_3$ reaction product.

The use of the Ln-Ln plots in the analysis of concentration dependent data derived from matrix isolation studies is based on the assumptions that the formation of a complex from two species striking the matrix surface simultaneously obeys a simple mass-action law. Thus the rate of formation of the complex is proportional to the product of the flux of the two species, and the order the metal dependence can be considered without concern for the actual rate. It should be noted the the use of this plot does not imply that all the metal has reacted or that one achieves a state of equilibrium.

Band d which results from the photolysis with UV (280 - 320 nm) light on a matrix containing Ga and H$_2$ is shown to contain one Ga atom. From the known optical spectra$^{(108)}$, Ga was excited from the $^2$P state to a $^2$D state by absorption at 292.0 nm which suggests that an energy barrier does exist for the insertion of ground state Ga into the H-H bond. Band d is observed at 1303.4 and 1245.1 cm$^{-1}$ in D$_2$ reactions and exhibits two peaks in HD reactions, with one at 1766.2 cm$^{-1}$ in the Ga-H stretching region and the other at 1269.6 cm$^{-1}$ in the Ga-D stretching region. In a HD reaction, only a single peak is present in the Ga-H stretching region and this peak is nearly bisecting the two peaks found in the H$_2$ reaction, which is also true in the
Ga-D stretching region. This fact strongly indicates that band d can be assigned to gallium dihydride, GaH₂. The peak at 1799.0 cm⁻¹ is thus assigned to the antisymmetric stretching (ν₃) mode and the peak at 1727.9 cm⁻¹ is assigned to the symmetric stretching (ν₁) mode for GaH₂. A shoulder for each of these peaks was observed and is thought to be due to different matrix sites because similar splitting is also observed for those peaks in HD and D₂ reactions. Two Ga-H stretching modes were also reported in the IR spectrum both in gas phase and in an inert gas matrix(88) for Ga₂H₆. The two IR bands were observed at 2015 (1996), and 1985 (1968) cm⁻¹ in an Ar matrix with the numbers in parentheses indicating different matrix sites. The higher vibration frequencies are not unexpected since the Ga-H bond length is expected to be shorter in Ga₂H₆ due to a larger positive charge present at the Ga centers.

Band a was indicated to involve two Ga atoms, and in a previous report(109) on reactions of gallium with water, this band was assigned to Ga₂H(OH) with both bridging H and bridging OH groups. However, from this study, only one peak at 1030 cm⁻¹ seems to have a correlation with the H₂O concentration as indicated in Fig. 5-4. The peaks at 1002.1 and 1015.8 cm⁻¹ do not appear to correlate with H₂O. Additionally, these peaks show a large shift in D₂ reactions and exhibit two bands with one in the Ga-H and one in the Ga-D regions in those reactions with HD. Thus we reassigned band a as Ga₂H₂ with two bridging hydrogens and no terminal hydrogens since no IR peaks in the terminal hydrogen region were seen to be in association with band a. Species a is thought to have the following structure:
Bonding may exist directly between Ga-Ga in species a. The appearance of these peaks in the previous study of reactions of gallium with water may result from the reactions of Ga$_2$ with small amount of impurity H$_2$ which is always present in the vacuum chamber either from the reaction of H$_2$O with the hot furnace surfaces or from the cracking of trace pump oil. The observed frequencies and their tentative assignments are listed in Table 5-1.

It has also been shown from the Ga concentration study that band c is also a diatomic Ga$_2$ related species which undergoes a large shift to 1206.5 cm$^{-1}$ in a D$_2$ reaction. In the HD reactions, two peaks at 1685.9 and 1206.5 cm$^{-1}$ were observed which are very close to the corresponding bands in Ga-H and Ga-D stretching regions observed for the H$_2$ and D$_2$ reactions, respectively. This strongly suggests that this species contains two individual Ga-H bonds which lack strong interactions. This species is thought to involve only one H$_2$ molecule because the intensities of the band c peaks do not appear to be appreciably affected by the change of H$_2$ flux at the matrix surface. Because the observed frequencies are in the terminal gallium-hydrogen stretching region, a molecule with two terminal Ga-H bonds is tentatively assigned with the following structure:

$$\text{H} \makebox[0.5cm]{---} \text{Ga} \makebox[0.5cm]{------} \text{Ga} \makebox[0.5cm]{---} \text{H}$$
where the Ga-Ga may contain some double bond character. However, whether the molecule is linear or bent is not certain. As shown in Fig. 5-1, bands a and c can be photolytically converted to each other according to the following reaction. The ability to convert the two species reversibly suggests that assignment to Ga$_2$ species with either bridging or terminal hydrogens.

\[
\text{Ga}_2(b-H)_2 \xrightleftharpoons{400-520 \text{ nm}}^{320-380 \text{ nm}} \text{Ga}_2(t-H)_2
\]

Bands b which include two peaks in the Ga-H stretching region shift to 1262.9 and 1276.2 cm$^{-1}$ in a D$_2$ reaction. In a HD reaction, two peaks were observed. A single peak at 1746.2 cm$^{-1}$ in the Ga-H stretching region and the other at 1262.9 cm$^{-1}$ in the Ga-D stretching region was observed. This is a typical pattern for the symmetric and antisymmetric stretchings for a triatomic molecule. It is also noted that the spacing (13 cm$^{-1}$) is much smaller than that of GaH$_2$ (72 cm$^{-1}$). This indicates that the interaction between the two Ga-H vibrations is much smaller than that in GaH$_2$. For the same reason mentioned above, band b is also thought to include only one hydrogen molecule. In conjunction with the fact that band b involves three Ga atoms, a molecule, Ga$_3$H$_2$, with the following geometry is tentatively assigned:

![Diagram of Ga$_3$H$_2$ molecule]
In this case two identical Ga-H bonds are well separated which results in very small coupling between them. Two peaks at 752.1 and 746.8 cm\(^{-1}\) observed in the H\(_2\) reactions also seem to relate with band b. They shift to 568.6 and 566.2 cm\(^{-1}\) in a D\(_2\) reaction. This may be attributed to some type of angle deformation.

As seen in Figs. 5-2 and 5-3, a peak at 1874.0 cm\(^{-1}\) is always present in the spectra for H\(_2\), D\(_2\), and HD reactions, and it was also noted from the gallium concentration study that it seems to involve more than one Ga atom. It is thought that this species results from spontaneous reactions of Ga\(_2\) with CO which results from the degassing of the cell and the gallium sample. One also notes that the peak at 822.1 cm\(^{-1}\) is not related to H\(_2\) either since it has already been reported earlier as Ga\(_2\)O\(^{111}\). This most likely comes from a certain amount of oxide in the gallium sample.

The reactions between Ga and H\(_2\), D\(_2\), HD have been studied in Kr matrices as well. A representation of the IR spectra for reactions with H\(_2\), HD, and D\(_2\) is given in Figures 5-7 and 5-8. As expected, the concentrations of Ga dimers and trimers are found to be much less than those seen for Ar matrices due to the higher rigidity of Kr matrices. The observed frequencies for GaH, GaH\(_2\), Ga\(_3\)H\(_2\), Ga\(_2\)(t-H\(_2\)), and Ga\(_2\)(b-H)\(_2\) can be found in Table 5-1 and 5-2. Surprisingly, the photolysis with UV (280 - 320, and 320 - 380 nm) which usually produced GaH\(_2\) in Ar matrices did not yield the intense peaks we assigned to the stretching modes for GaH\(_2\). Only GaH (at 1507.6 cm\(^{-1}\)) was seen to grow dramatically after UV photolysis as seen in Fig. 5-7. This peak is observed to shift to 1086.5 cm\(^{-1}\) for GaD. Also, although the intensity for GaH is higher that that of GaH\(_2\), it is still much smaller than that in an Ar matrix. The assigned Ga\(_2\)(CO) was observed to
Figure 5-7. IR spectra for reactions of gallium with hydrogen in Kr matrices after photolysis with $\lambda > 450$ nm light for 10 minutes.

(A) with $\text{H}_2$;
(B) with $\text{HD}$;
(C) with $\text{D}_2$. 
Figure 5-8. IR spectra for reactions of gallium with hydrogen in Kr matrices. All spectra were recorded after photolysis with UV (270-380 nm) light for 10 minutes.

(A) with H₂;
(B) with HD;
(C) with D₂.
occur at 1872.5 cm\(^{-1}\) and Ga\(_2\)O at 815.5 cm\(^{-1}\) in a Kr matrix. The formation of lesser amounts of gallium-hydrogen products is thought to be due to the possibility that krypton binds more strongly than does argon, thus inhibiting the formation of the hydrogen complex. The observed frequencies for the reaction products in Kr matrices are also listed in Tables 5-1 and 5-2.
Table 5-1. The Observed Frequencies (cm\(^{-1}\)) for Ga\(_x\)H\(_y\)

<table>
<thead>
<tr>
<th></th>
<th>GaH(_2)</th>
<th>GaD(_2)</th>
<th>GaHD</th>
</tr>
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<tr>
<td></td>
<td>Kr</td>
<td>Ar</td>
<td>Kr</td>
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<tr>
<td>asym</td>
<td>1796.4</td>
<td>1799.1</td>
<td>1302.4</td>
</tr>
<tr>
<td></td>
<td>(0.57)(^a)</td>
<td></td>
<td>(0.66)</td>
</tr>
<tr>
<td>sym</td>
<td>1730.8</td>
<td>1727.9</td>
<td>1244.2</td>
</tr>
<tr>
<td></td>
<td>(0.09)</td>
<td></td>
<td>(0.11)</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>GaH</th>
<th>GaD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1507.6</td>
<td>1514.1</td>
</tr>
<tr>
<td>1086.5</td>
<td>1090.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ga(_3)H(_2)</th>
<th>Ga(_3)D(_2)</th>
<th>Ga(_3)HD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kr</td>
<td>Ar</td>
</tr>
<tr>
<td>1740.4</td>
<td>1752.8</td>
<td>1253.3</td>
</tr>
<tr>
<td>1753.2</td>
<td>1765.8</td>
<td>1267.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ga(_2)(b-H)(_2)</th>
<th>Ga(_2)(b-D)(_2)</th>
<th>Ga(_2)(b-HD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga-H</td>
<td>1022.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1002.1(^b)</td>
<td></td>
</tr>
<tr>
<td>Ga-D</td>
<td>743.0</td>
<td>728.2</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>728.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ga(_2)(t-H)(_2)</th>
<th>Ga(_2)(t-D)(_2)</th>
<th>Ga(_2)(t-HD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga-H</td>
<td>c</td>
<td>1686.2</td>
</tr>
<tr>
<td>Ga-D</td>
<td>1218.2</td>
<td>1206.5</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>1685.9</td>
</tr>
<tr>
<td></td>
<td>1219.0</td>
<td>1206.5</td>
</tr>
</tbody>
</table>

\(^a\) The numbers in parentheses provide a relative measurement of the intensities of the two stretching modes.

\(^b\) Indicates the strongest peak in the band.

\(c\) Indicates that the peak is too weak to observe.
Table 5.2. Reaction Product Absorptions (cm\(^{-1}\)) for Reactions of Gallium with Hydrogen in Ar and Kr matrices.

<table>
<thead>
<tr>
<th>obs. frequencies (cm(^{-1}))</th>
<th>assignments</th>
<th>label</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>Kr</td>
<td></td>
</tr>
<tr>
<td>1874.0</td>
<td>1872.5</td>
<td>Ga(_2)(CO)(_x)</td>
</tr>
<tr>
<td>1799.0, 1727.9</td>
<td>1796.4, 1730.8</td>
<td>GaH(_2)</td>
</tr>
<tr>
<td>1766.2, 1269.6</td>
<td>1763.6, 1261.2</td>
<td>GaHD</td>
</tr>
<tr>
<td>1670.0</td>
<td>1665.0</td>
<td>H-GaOH</td>
</tr>
<tr>
<td>1575.0</td>
<td>1570.5</td>
<td>Ga(OH(_2))</td>
</tr>
<tr>
<td>1514.1</td>
<td>1507.6</td>
<td>GaH</td>
</tr>
<tr>
<td>1686.2</td>
<td></td>
<td>Ga(_2)(t-H)(_2)</td>
</tr>
<tr>
<td>1685.9, 1206.5</td>
<td></td>
<td>Ga(_2)(t-HD)</td>
</tr>
<tr>
<td>1752.8, 1765.8</td>
<td>1740.4, 1753.2</td>
<td>Ga(_3)(t-H)(_2)</td>
</tr>
<tr>
<td>1759.0, 1262.9</td>
<td>1746.2, 1260.5</td>
<td>Ga(_3)(t-HD)</td>
</tr>
<tr>
<td>1262.9, 1276.2</td>
<td>1253.3, 1267.2</td>
<td>Ga(_3)(t-D)(_2)</td>
</tr>
<tr>
<td>1206.5</td>
<td>1218.2</td>
<td>Ga(_2)(t-D)(_2)</td>
</tr>
<tr>
<td>1090.3</td>
<td>1086.5</td>
<td>GaD</td>
</tr>
<tr>
<td>1002.1</td>
<td>1022.3</td>
<td>Ga(_2)(b-H)(_2)</td>
</tr>
<tr>
<td>822.4</td>
<td>815.5</td>
<td>Ga(_2)O</td>
</tr>
<tr>
<td>728.2</td>
<td>704.6</td>
<td>Ga(_2)(b-D)(_2)</td>
</tr>
<tr>
<td>952.7, 680.1</td>
<td>953.1, 655.0</td>
<td>Ga(_2)(b-HD)</td>
</tr>
</tbody>
</table>
5.3.2. Reactions of Gallium with Methane

Fig. 5-9 shows a collection of the IR spectra of the photoreaction products in a matrix containing Ga and CH$_4$ in an excess of Ar. It is noticed that a small amount H$_2$ does exist in the system which was indicated by the presence of several peaks described previously in the hydrogen reactions. Photolysis with light of $\lambda > 400$ nm causes only the growth of several hydrogen and gallium cluster related species. The exposure of the matrix to UV (320-380 nm) light produced two peaks in the Ga-H stretching region, one at 1670.0 cm$^{-1}$ which has been previously assigned to HGaOH, the other one at 1719.7 cm$^{-1}$ which exhibits a large shift in CD$_4$ reactions, and almost no change in a reaction with $^{13}$CH$_4$ as illustrated in Fig. 5-10. This peak is thought to result from the insertion of Ga into H-C bond in CH$_4$. This peak is readily removed when the same matrix was photolyzed with light of $\lambda > 580$ nm, which suggests that this reaction product has an absorption in $\lambda > 580$ nm region. A decomposition product is not observed; however, it was reported$^{(112)}$ in studies of reactions of Al with CH$_4$ that HAICH$_3$ reverts to Al and CH$_4$. A similar reaction is also expected for HGaCH$_3$. In addition, gallium and methane concentration studies revealed that this species only involved one Ga atom and one CH$_4$ molecule, which also supports this assignment. A second peak at 528.6 cm$^{-1}$ for a CH$_4$ reaction shifted to 515.0 cm$^{-1}$ for a $^{13}$CH$_4$ reaction but underwent only a small shift for a CD$_4$ reaction. This peak is thought to be due to the Ga-C stretching mode. Ga-C stretching modes have been observed$^{(106)}$ at 526 and 576 cm$^{-1}$ for Ga(CH$_3$)$_3$, and at 520 and 565 cm$^{-1}$ for the adduct Ga(CH$_3$)$_3$·AsH$_3$. It is also noted that
Figure 5-9. Infrared spectra for a matrix with Ga and CH$_4$ in an excess of Ar.

(A) on deposition;
(B) following photolysis with light of $\lambda > 450$ nm for 10 minutes;
(C) following subsequent photolysis of $270 \text{ nm} < \lambda < 380$ nm for 10 minutes;
(D) following subsequent photolysis of $\lambda > 580$ nm for 10 minutes;
(E) following subsequent photolysis of $270 \text{ nm} < \lambda < 380$ nm for 10 minutes.

a = HGaCH$_3$. 
Fig. 5-10. A summary of IR spectra of reactions of gallium with methane in Ar matrices after photolysis of UV (270 - 380 nm) for 10 minutes.

(A) with CH\textsubscript{4};
(B) with CD\textsubscript{4};
(C) with \textsuperscript{13}CH\textsubscript{4}.

\textit{a = methylgallium hydride.}
a peak at 754.3 cm\(^{-1}\) in a CH\(_4\) reaction shifted slightly to 748.7 cm\(^{-1}\) in a \(^{13}\)CH\(_4\) reaction, and that it also exhibited a large shift to 578.3 cm\(^{-1}\) in a CD\(_4\) reaction. They have been assigned to a methyl rocking mode, \(\rho(\text{CH}_3)\). Several other anticipated C-H stretching, and \(\delta(\text{CH}_3)\) for methylgallium hydride were either too weak to observe or obscured by strong absorptions of parent CH\(_4\) as noted in Table 5-3. Unlike the reactions with H\(_2\), the concentration studies indicate that no reactions due to small clusters, such as Ga\(_2\), Ga\(_3\), with CH\(_4\) were observed. A series of reactions with different concentrations of CH\(_4\) has been carried out in Ar matrices; no reactions due to more than one CH\(_4\) molecule were seen to occur either.

The reactions of gallium with methane were also examined in Kr matrices and pure methane matrices. Weak absorptions for HGaCH\(_3\) were identified. The observed frequencies and their assignments are summarized in Table 5-3. The relative intensities of the assigned modes seem to be matrix dependent presumably because of the different interactions of methylgallium hydride, CH\(_3\)GaH, with the matrix materials. Even in pure methane matrices atomic gallium was not observed to react with more than one CH\(_4\) molecule.
<table>
<thead>
<tr>
<th></th>
<th>Ar</th>
<th>Kr</th>
<th>Methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-GaCH$_3$</td>
<td>1719.7</td>
<td>1712.5</td>
<td>1709.6</td>
</tr>
<tr>
<td>H-Ga$^{13}$CH$_3$</td>
<td>1719.7</td>
<td>1712.7</td>
<td>1705.7</td>
</tr>
<tr>
<td>D-GaCD$_3$</td>
<td>1243.6</td>
<td>1239.0</td>
<td>1285.8</td>
</tr>
<tr>
<td>HGa-CH$_3$</td>
<td>528.6</td>
<td>520.0</td>
<td>524.0</td>
</tr>
<tr>
<td>HGa-$^{13}$CH$_3$</td>
<td>515.4</td>
<td>a</td>
<td>519.2</td>
</tr>
<tr>
<td>DGa-CD$_3$</td>
<td>525.0</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>$\rho$(CH$_3$)</td>
<td>753.1</td>
<td>747.8</td>
<td>768.9</td>
</tr>
<tr>
<td>$\rho$(CH$_3$)</td>
<td>748.7</td>
<td>746.8</td>
<td>745.3</td>
</tr>
<tr>
<td>$\rho$(CD$_3$)</td>
<td>578.2</td>
<td>a</td>
<td>589.8</td>
</tr>
<tr>
<td>$\delta$(CH$_3$)</td>
<td>1176.4</td>
<td>1153.7</td>
<td>1153.7</td>
</tr>
<tr>
<td>$\delta$(CH$_3$)</td>
<td>a</td>
<td>1153.5</td>
<td>1146.0</td>
</tr>
<tr>
<td>$\delta$(CD$_3$)</td>
<td>a</td>
<td>747.0</td>
<td>786.0</td>
</tr>
</tbody>
</table>

a. Indicates band too weak to observe or obscured by strong parent methane absorptions.
5.3.3. Germanium with Hydrogen

Germanium has been cocondensed with molecular hydrogen in Ar and Kr matrices. It has been found that atomic germanium reacts with molecular hydrogen spontaneously at 12K to produce germylene, GeH₂, which is similar to the studies on reactions of silicon with H₂\(^{110}\). The insertion product, GeH₂, further reacts with excess hydrogen to give germane, GeH₄. However, the formation of GeD₄ is not seen in reactions with D₂, likely due to the lower mobility for D₂ than for H₂. The observed vibrational frequencies and their assignments are summarized in Table 5-4. Since germanium hydrides such as GeH₂, GeH₄, and Ge₂H₆ have been previously characterized both experimentally\(^{113}\) and theoretically\(^{114}\), the infrared spectra for reactions of germanium with hydrogen are omitted here. As seen in Table 5-5, the observed frequencies are in good agreement with literature values. Digermane(Ge₂H₆) is produced presumably from the insertion of GeH₂ into GeH₄. Photolysis with UV(280 - 370 nm) has no effect on the GeH₂ and GeH₄; however, it decreases the intensity for Ge₂H₆.

The observation of both symmetric and antisymmetric stretching modes for GeH₂ indicates that GeH₂ has a bent geometry too.
Table 5-4. The Observed Frequencies (cm$^{-1}$) for Ge$_x$H$_y$

<table>
<thead>
<tr>
<th></th>
<th>GeH$_2$</th>
<th></th>
<th>GeD$_2$</th>
<th></th>
<th>GeHD</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Kr</td>
<td>Ar</td>
<td>Kr</td>
<td>Ar</td>
<td>Kr</td>
<td>Ar</td>
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<tr>
<td>asym stretching</td>
<td>1873.3</td>
<td>1860.0</td>
<td>1355.9</td>
<td>1342.2</td>
<td>Ge-H</td>
<td>1875.4</td>
</tr>
<tr>
<td></td>
<td>1855.7</td>
<td></td>
<td>1336.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sym stretching</td>
<td>1879.3</td>
<td>1843.1</td>
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<td>1330.4</td>
<td>Ge-D</td>
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</tr>
<tr>
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<td></td>
<td>1325.1</td>
<td></td>
<td></td>
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<tr>
<td>bending</td>
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<td>898.7</td>
<td>629.2</td>
<td>626.2</td>
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<td>757.9</td>
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<table>
<thead>
<tr>
<th></th>
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<th>GeD$_4$</th>
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<th>GeH$_2$D$_2$</th>
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<tr>
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<td>816.7</td>
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<td>1527.3</td>
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<table>
<thead>
<tr>
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<th>Ge$_2$(t-H)$_2$</th>
<th></th>
<th>Ge$_2$(t-D)$_2$</th>
<th></th>
<th>Ge$_2$(t-HD)</th>
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<td>1831.6</td>
</tr>
<tr>
<td>Ge-D</td>
<td>1347.5</td>
<td>1320.5</td>
<td>1347.3</td>
<td>1316.9</td>
<td></td>
<td></td>
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</tbody>
</table>
Table 5-5. Comparison between observed frequencies with literature values for germanium hydrides in Ar matrices.

<table>
<thead>
<tr>
<th>Observed</th>
<th>Literature&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
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<td>2098.2, 816.7</td>
<td>2097, 812</td>
<td>GeH₄</td>
</tr>
<tr>
<td>2090.5, 1514.1, 656</td>
<td>2097, 1542, 766, 651</td>
<td>GeH₂D₂</td>
</tr>
<tr>
<td>2089.4, 897.0</td>
<td>2099, 878</td>
<td>Ge₂H₆</td>
</tr>
<tr>
<td>1860, 1843, 898</td>
<td>1887, 1864, 920</td>
<td>GeH₂</td>
</tr>
<tr>
<td>1855.4, 1339.1, 764.6</td>
<td>1861, 1329, 806</td>
<td>GeHD</td>
</tr>
<tr>
<td>b</td>
<td>1540, 1513, 595</td>
<td>GeD₄</td>
</tr>
<tr>
<td>1342.2, 1330.4, 646</td>
<td>1338, 1325, 658</td>
<td>GeD₂</td>
</tr>
</tbody>
</table>

<sup>a</sup> from reference 112.

<sup>b</sup> not observed in this study.
5.4. DISCUSSION

It is interesting to note the different behaviors of the main group metals, e.g., gallium, germanium, and aluminum, etc., and most of the transition metals with respect to reaction with hydrogen in either an argon or a krypton matrix. For transition metals as described in previous chapters, the MH$_2$ product was always found to be favored in a krypton matrix relative to an argon matrix. As noted earlier in this chapter, however, the opposite case is found for gallium and germanium. In general, one expects more metal atoms to be available in a krypton matrix than in an argon matrix due to reduced metal cluster formation at the same metal concentrations. This normally results in increased metal atom-hydrogen reaction. However, if complexation of molecular hydrogen with the metal atom does not compete favorably with the interaction of metal with the matrix atom, the formation of hydrogen complex will be reduced; therefore, the photoreaction products between the metal and hydrogen will be decreased. This is apparently the case for gallium. The lack of interacting d-orbitals for the main group metals reduces the interaction of dihydrogen to more of a Van der Waals type of interaction. Thus, the more polarizable krypton is able to interact more strongly with gallium than dihydrogen. For most of the transition metals, on the other hand, the low lying d-orbitals are available and the interaction with dihydrogen is no longer only Van der Waals in nature and thus, dihydrogen is able to compete favorably with krypton with respect to formation of a complex.

Table 5-6 lists some known molecules with terminal Ga-H and Ge-H bonds and their vibration frequencies. The stretching force constants for
the Ga-H and Ge-H stretching have been calculated with a diatomic approximation using the vibration frequencies for the H-Ga and D-Ga stretchings. We believe that the comparison of the H-Ga and Ge-H force constants can throw some light to the nature of the bonds or to the electronic structure of the molecules. The large observed differences in frequencies and force constants between GaH and GaH₂ is of interest. The major cause for this difference is likely due to the increased s-orbital participation in the bonding. The bonding in GaH₂ is likely to be a combination of sp² and sp bonding while that for GaH is essentially a combination of p and sp bonding. Consequently, the bond distance for GaH₂ is expected to be shorter than that for GaH since the s orbital is a more contracted orbital. The participation of s-orbital in the bonding framework also increases the overlap energy. It is also possible that the much weaker Ga-H bond for GaH than for GaH₂ is a result of promotion energy. For GaH₂ the promotion energy is shared by two Ga-H bonds. It is noticed that the force constants of HMD (M = Ga and Ge) are smaller than those of HMOH (M = Ga and Ge), which indicates that having electron withdrawing group (hydroxyl) slightly weakens the H-M bonds.

The bond angles for species such as Ga₃H₂ and Ga₂(b-H)₂, and Ga₂(t-H)₂ can not be determined from the limited informations obtained in this study. Further understanding of the molecules will benefit greatly from quantum mechanic calculations. The bond angle for GaH₂, however, can be estimated through the measured relative intensities of the symmetric and antisymmetric stretching modes, where one assumes that the relative transition moments are a vectorial sum of the dipole moment changes of the individual metal-hydrogen bonds. The relative intensities for GaH₂
which were obtained from integration of peak areas are listed in Table 5-1 together with the frequencies.

A result of $136^\circ$ for $2\theta$ is obtained in an Ar matrix using the relative intensities of GaH$_2$. For GaD$_2$, the bond angle is calculated to be $135^\circ$. No attempt was made to determine the bond angle for GaH$_2$ in a Kr matrix because the peaks are too weak to be measured accurately. The uncertainty in measurements of peak intensities and the assumption made for using the above equation is believed to be small and an upper limit of $\pm 5^\circ$ of error in the bond angle measurement is suggested. A bond angle of $136^\circ$ suggests partial sp and sp$^2$ bonding in GaH$_2$. If one assumes sp bonding is linear and sp$^2$ produces a bond angle of $120^\circ$ and a linear relationship exists between bond angle and s, p character, then we calculate 38% s and 62% p character for GaH$_2$.

The symmetric and antisymmetric stretching modes for GeH$_2$ have similar intensities. A bond angle of $95^\circ$ is obtained for GeH$_2$ in an Ar matrix. The smaller bond angle for GeH$_2$ than for GaH$_2$ is probably due to larger p character in the Ge-H bonds.

The geometry of methylgallium hydride, HGaCH$_3$, is expected to be similar to that for GaH$_2$, due to the common character of the methyl and hydride groups with respect to Ga single bond formation.
Table 5-6. Comparisons of Terminal H-Ga and H-Ge Bonds Among Observed Species in Ar Matrices

<table>
<thead>
<tr>
<th></th>
<th>$\omega^H_\text{H}(\text{cm}^{-1})$</th>
<th>$\omega^H_\text{e}(\text{cm}^{-1})$</th>
<th>$\omega^H_\text{e}^H_\text{e}(\text{cm}^{-1})$</th>
<th>$k_{\text{M-H}}(\text{mdyn} / \text{Å})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Ga$^{(a)}$</td>
<td>1546.9</td>
<td>1604.5</td>
<td>28.8</td>
<td>1.51</td>
</tr>
<tr>
<td>H-Ga</td>
<td>1514.1</td>
<td>1570.9</td>
<td>28.4</td>
<td>1.44</td>
</tr>
<tr>
<td>H-GaD</td>
<td>1766.2</td>
<td>1823.0</td>
<td>28.9</td>
<td>1.95</td>
</tr>
<tr>
<td>H-GeD</td>
<td>1846.3</td>
<td>1932.9</td>
<td>43.3</td>
<td>2.18</td>
</tr>
<tr>
<td>H-GaOH$^{(b)}$</td>
<td>1669.8</td>
<td>1791.5</td>
<td>60.9</td>
<td>1.89</td>
</tr>
<tr>
<td>H-GeOH$^{(c)}$</td>
<td>1741.2</td>
<td>1832.8</td>
<td>45.8</td>
<td>1.97</td>
</tr>
<tr>
<td>H-GaCH$_3$</td>
<td>1719.7</td>
<td>1818.6</td>
<td>49.4</td>
<td>1.94</td>
</tr>
<tr>
<td>H-Ga$_2$H$_5$</td>
<td>1985, 2015</td>
<td>2039, 2069</td>
<td>$-27.0$</td>
<td>2.47</td>
</tr>
<tr>
<td>H-GeH$_3$</td>
<td>2099</td>
<td>2192</td>
<td>46.4</td>
<td>2.81</td>
</tr>
</tbody>
</table>

5.5. **SUMMARY**

Gallium atoms do not react with H\textsubscript{2} and CH\textsubscript{4} in their ground state. Excited atomic gallium was found to insert into the H-H bonds to produce GaH and GaH\textsubscript{2}. The dimer of gallium, Ga\textsubscript{2}, forms a hydride with bridging hydrogens upon condensation in Ar matrices. Molecules such as Ga\textsubscript{2}(t-H)\textsubscript{2} and Ga\textsubscript{3}(t-H)\textsubscript{2} were produced by photolysis with UV( 320 - 380 nm) light. Atomic gallium also inserts into the C-H bond of CH\textsubscript{4} to form HGaCH\textsubscript{3} upon photolysis with UV light.

The observed reactions in this study can be summarized as follows:
Ga + H₂

Ga₂H₂

Ga₂ + H₂ \xrightarrow{UV(280-370\text{nm})} \rightarrow Ga₂(b-H)₂

Ga₂(b-H)₂ \xrightarrow{400 - 520 \text{ nm}} \leftrightarrow 320 - 380 \text{ nm} \rightarrow Ga₂(t-H)₂

Ga₃ + H₂ \xrightarrow{400 - 520 \text{ nm}} \leftrightarrow 320 - 380 \text{ nm} \rightarrow Ga₃(t-H)₂

Ga + CH₄

Ga + CH₄ \xrightarrow{320 - 380 \text{ nm}} \leftrightarrow \lambda > 580 \text{ nm} \rightarrow HGaCH₃

Ge + H₂

GeH₂

Ge₂H₆ \xrightarrow{GeVH₂} \rightarrow GeH₄
Chapter VI

CONCLUSIONS

6.1. Molecular Orbital Considerations

Reactions of the first row transition metals with molecular hydrogen have been investigated via FT-IR matrix-isolation spectroscopy. The generally observed reaction is the insertion reaction (6-1) which involves the breakage of the H-H bond and the formation of two M-H bonds.

\[ \text{M} + \text{H}_2 \rightarrow \text{MH}_2 \quad (6-1) \]

An energy barrier has been found for most of the first row transition metals (from Ca to Zn, with Ni\(^{(80)}\) being an exception), i.e., the metals do not react with H\(_2\) in their ground states. Reaction (6-1) is usually endothermic for most of the metals since the H-H bond has a bond energy of 104 kcal/mol, and many M-H bonds have bond energies less than 52 kcal/mol. It is interesting to note that the spontaneous reaction of Ni implies a lower limit of 52 kcal/mol bond energy for NiH\(_2\).

For the first row transition metals the valence orbitals are the 3d, 4s, and 4p orbitals in order of increasing energy. For single metal atom insertion into the H-H bond there are two requirements for a low energy barrier path\(^{(116)}\): first, the metal atom must have a d\(^{n+1}\)s state, which includes open shell d-orbitals; and secondly, a singly occupied d-orbital must be low-spin coupled to the single 4s electron. The low-spin coupling requirement allows an efficient sd hybridization which will reduce the repulsion between the doubly occupied \(\sigma\)-orbital of H\(_2\) and the metal atom as
H₂ approaches. The singly occupied d-orbital and the singly occupied s-orbital can begin to form the two new metal-hydrogen bonds as the H₂ bond breaks. The unexpectedly high reactivity of atomic Ni with regard to the insertion of the H-H bond is most likely due to its low lying d⁹s¹ electronic configuration, which is only 9.8 kcal/mol above the ground state and also fulfills the two previously stated requirements.

For most first-row transition metals, the formation of MH₂ does not accompany the production of metal monohydrides, MH. The formation of MH₂ is thought to proceed by a concerted reductive pathway in a C₂ᵥ symmetry. The efficient interaction between metal atoms with dihydrogen in a C₂ᵥ symmetry can be described by Fig. 6-1. Initially, the fully occupied σg orbital of H₂ interacts with the σ(4s) orbitals from the metal center to form bonding and antibonding MOs, where the bonding orbital is doubly occupied and antibonding orbital singly occupied which leads to a net bonding interaction. It is clear that when the metal 4s orbital is doubly occupied the interaction of the metal 4s orbital and the σg orbital of H₂ leads to double occupancy of the antibonding orbital. This can explain why most transition metals in their ground states (ns²) do not spontaneously insert into the H-H bond. As also indicated by Fig. 6-1 the reaction is favored by increasing electron donation from the metal π(3d) orbital to the antibonding σ* orbital of H₂ upon closer approach of H₂.

For those post transition metals (such as Ga, Ge, etc), the reactive excited states are thought to be low spin coupled sp states. Similar arguments can be made as above for a low reactin barrier to bond insertion into H₂, as well as for low reactivity of Ga in its ground state.
Figure 6-1. Orbital interactions for the $\sigma$ and $d\pi$ orbitals of M with the molecular orbitals of $H_2$ in $C_{2v}$ symmetry.
6.2. Stretching Force Constants of MH$_2$

As described in Chapter I, the bond angles for MH$_2$ can be estimated through the relative intensities of the antisymmetric and symmetric stretching modes and the stretching force constants can be calculated with a diatomic approximation the the M-H and M-D vibrational frequencies of MHD. The observed frequencies and calculated stretching force constants, bond angles are summarized in Table 6-1.

Figure 6-2 displays the plot of stretching force constants of MHD versus the atomic number, where the values for HMOH are also plotted for comparison. The stretching force constants for both HMD and HMOH$^{(117)}$ are seen to increase across the series (from Ca to Zn). This is undoubtedly due to the regular reduction in the metal radius with increasing atomic number across the series. If a line is drawn, as shown in Fig. 6-2, between Ca and Zn, for MH$_2$ species the deviation from the line for ScH$_2$, TiH$_2$, VH$_2$ and CrH$_2$ is seen to increase through this series. The deviation from the line for the first half transition metals suggests that 3d orbitals of the metals are participating significantly in the bonding. However, MnH$_2$ has a smaller force constant than CrH$_2$. The discontinuity form CrH$_2$ to MnH$_2$ presumably is due to the stable ground state (3d$^5$4s$^2$) of Mn and a large promotion energy from its ground state to a reactive sd state. The bonding for MnH$_2$ principally utilizes sp hybridized orbitals.

It is also noticed in Figure 6-2 that NiH$_2$ has a unusual large force constant. This can also be explained by the low lying $^1$D(d$^9$s) state of Ni. Large 3d involvement is believed to exist in the Ni-H bonds of NiH$_2$. A short bond length is expected for NiH$_2$, since the 3d orbitals of Ni are significantly
Table 6-1. The M-H Force Constants and Bond Angles for the MHD of First-row Transition Metals

<table>
<thead>
<tr>
<th>metal</th>
<th>$\omega^H$ (cm$^{-1}$)</th>
<th>$\omega^D$ (cm$^{-1}$)</th>
<th>$\omega^H_xe^H$ (cm$^{-1}$)</th>
<th>$\omega^D_xe^H$ (cm$^{-1}$)</th>
<th>$\omega^D_xe^D$ (cm$^{-1}$)</th>
<th>$k_{M-H}$ (mdyn/Å)</th>
<th>$\theta$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>1228.4</td>
<td>882.0</td>
<td>1240.8</td>
<td>888.4</td>
<td>6.2</td>
<td>3.2</td>
<td>0.89</td>
</tr>
<tr>
<td>Sc</td>
<td>1348.7</td>
<td>967.4</td>
<td>1363.3</td>
<td>974.8</td>
<td>7.3</td>
<td>3.7</td>
<td>1.08</td>
</tr>
<tr>
<td>Ti</td>
<td>1447.8</td>
<td>1043.0</td>
<td>1488.7</td>
<td>1063.9</td>
<td>20.45</td>
<td>10.4</td>
<td>1.29</td>
</tr>
<tr>
<td>V</td>
<td>1518.2</td>
<td>1095.6</td>
<td>1573.4</td>
<td>1123.8</td>
<td>27.6</td>
<td>14.1</td>
<td>1.44</td>
</tr>
<tr>
<td>Cr</td>
<td>1627.1</td>
<td>1174.4</td>
<td>1689.1</td>
<td>1206.0</td>
<td>31.0</td>
<td>15.8</td>
<td>1.64</td>
</tr>
<tr>
<td>Mo</td>
<td>1720.0</td>
<td>1234.7</td>
<td>1776.8</td>
<td>1263.4</td>
<td>28.4</td>
<td>14.4</td>
<td>1.86</td>
</tr>
<tr>
<td>Mn$^a$</td>
<td>1618.0</td>
<td>1160.0</td>
<td>1643.4</td>
<td>1172.9</td>
<td>12.7</td>
<td>6.46</td>
<td>1.58</td>
</tr>
<tr>
<td>Fe$^b$</td>
<td>1691.0</td>
<td>1215.0</td>
<td>1731.4</td>
<td>1235.6</td>
<td>20.2</td>
<td>10.3</td>
<td>1.75</td>
</tr>
<tr>
<td>Co$^c$</td>
<td>1715.0</td>
<td>1235.0</td>
<td>1772.1</td>
<td>1264.0</td>
<td>28.5</td>
<td>14.5</td>
<td>1.83</td>
</tr>
<tr>
<td>Ni$^d$</td>
<td>1967.0</td>
<td>1421.0</td>
<td>2054.4</td>
<td>1465.5</td>
<td>43.7</td>
<td>22.2</td>
<td>2.46</td>
</tr>
<tr>
<td>Cu$^e$</td>
<td>1861.0</td>
<td>1340.0</td>
<td>1927.4</td>
<td>1373.7</td>
<td>33.2</td>
<td>16.9</td>
<td>2.17</td>
</tr>
<tr>
<td>Zn</td>
<td>1766.2</td>
<td>1230.0</td>
<td>1824.0</td>
<td>1299.4</td>
<td>28.9</td>
<td>14.7</td>
<td>1.95</td>
</tr>
<tr>
<td>Ge</td>
<td>1846.3</td>
<td>1332.7</td>
<td>1932.9</td>
<td>1376.6</td>
<td>43.3</td>
<td>21.9</td>
<td>2.18</td>
</tr>
</tbody>
</table>

a, b, c, d, and e are from references 120, 121, 122, 79, and 123, respectively.
Figure 6-2. Plot of the stretching force constants of H-MD and H-MOH species versus atomic number.
smaller than the Ni 4s orbitals due to their lower principal quantum number.

Figure 6-2 also displays the stretching force constants for HMoD, HMeD\textsuperscript{118}, and HAlD\textsuperscript{119}, which provide a comparison among similar species within same group. For main group metals (groups IIA and IIIA), from top to bottom, the atomic radius increases and the electronegativity decreases as the atomic number increases. The M-H bonds are thus expected to become more ionic as the atomic number increases. The difference between HCrD and HMoD has been described in Chapter III, and can be explained by the greater participation of more d orbitals for second-row transition metals as compared to the first row transition metals.

It is of interest to note that for most transition metals (from Ca to Zn) the H-M bonds in HMOH species have larger force constant than the H-M bonds in HMD species, however, the force constants for H-GaOH and HGeOH are smaller than their respective hydrides, HMD (M=Ga and Ge). In general, one expects that an increase in ionic character of a bond is expected to decrease the force constant of the bond because the coulombic force is a longer range force even though the bond energy may increase. For the transition metals, it is likely that the initially significantly ionic hydride bond becomes less ionic in H-MOH than in H-MH, most likely due to the increased electron withdrawing ability of the hydroxyl group relative to a second hydrogen. The gallium hydrogen bond is likely to be less ionic due to the higher electronegativity of gallium relative to the transition metals. It is possible that the reduction in the force constant for the H-GaOH bond relative to H-GaD and H-GaCH\textsubscript{3} results from an actual
weakening of the hydrogen bond in H-GaOH due to greater tendency toward the H(\(^3\)GaOH) electronic state. The unit valency state for the group IIIA metals is commonly observed in the vapor state. The inversion of the ionic state to an acidic condition with the hydrogen positively charged is also a possible explanation for the bond force constant decrease in the H-GaOH. In this case one expects a similar behavior for the H-GeOH species.

6.3. Bond Angles of MH\(_2\)

Two models are employed to explain the bent nature for MH\(_2\) (M = transition metals). Firstly, the bent nature can be explained by the participation of d orbitals in the covalent bonding for transition metals. The alternative model emphasizes the polarization of the large M\(^{2+}\) cations by the anions as the main driving force for the bending. From this study we conclude that the involvement of 3d orbitals in bonding of M-H is the main reason for the bent nature of MH\(_2\). The bond angles change from 169° for CaH\(_2\) to 118° for CrH\(_2\) and increase to 180° for MnH\(_2\), which strongly suggests that there exists a correspondence between the bond angle and the involvements of 3d orbitals. The unexpectedly small bond angle 110° for ScH\(_2\) is thought to be a consequence of comparable sizes of the 4s and 3d orbitals and of bonding from sd hybrids. The bond angle for NiH\(_2\) is calculated to be 90°, which is also thought to result from the large 3d-character in the bonding.

For those post transition metals (such as Ga, Ge, etc.), 3d orbitals are fully occupied and become core orbitals. 4s and 4p orbitals are the outmost orbitals. The bent geometry for the dihydrides of these metals can not be
explained by the participation of 3d orbitals. Instead, the metal center can utilize both sp and sp\(^2\) hybridization to form two M-H bonds. The bent nature is thought to be a result from increased p character in the bonding.
REFERENCES


(80). M. Park, Ph.D dissertation, 1988, Rice University, Houston, TX.


