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Cryogenic Reactions of Gallium with Molecular Hydrogen and Methane

Z. L. Xiao, R. H. Hauge, and J. L. Margrave*

Department of Chemistry and Rice Quantum Institute, Rice University, P. O. Box 1892,
Houston, Texas 77251

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The reactions of gallium with molecular hydrogen and methane have been investigated via FT-IR matrix isolation spectroscopy. It is found that excited atomic gallium reacts with H_2 to yield both GaH and GaH_2, where GaH_2 is identified as a bent molecule with a bond angle of 136 ± 5°. The dimer of gallium, Ga_2, reacts spontaneously with H_2 to form $Ga_2(b\text{-}H)_2$ with two bridging hydrogens, which can be converted photoreversibly to $Ga_2(t\text{-}H)_2$ with two terminal hydrogens. The trimer of gallium, Ga_3, has also been isolated and found to react with H_2. The reactions of Ga with CH_4 have also been studied in Ar, Kr, and neat CH_4 matrices. $HGaCH_3$ was the only photoreaction product identified.

Introduction

Gallium hydrides have been actively studied throughout the last several decades.[1,2] Recently, the infrared spectra of isotopic species of gallium hydride, ^{69}GaH,[3] ^{71}GaH,[3] and GaD[4] were extensively reinvestigated by Jones et al. using a diode laser spectrometer. The recent success[5] in the synthesis of digallane (Ga_2H_6) by Downs, Goode, and Pulham is of great importance, since little was known about the structural properties and the stability of this molecule.

Because of its tremendous importance in the semiconductor industry, the synthesis of gallium-related compounds such as GaAs, GaAsAl, etc. has been extensively investigated. Trimethylgallium (TMG)[6] and triethylgallium (TEG) are widely used precursors in CVD processes leading to these materials. The $Ga(CH_3)$[7] radical has been directly detected by Stuke et al. with a mass spectrometer, where $Ga(CH_3)$ is produced as a UV laser fragment from gaseous TMG. A β-elimination scheme in which an H–Ga bond was formed was proposed for the decomposition of $Ga(C_2H_5)_3$.[8] The general interest in gallium chemistry suggests that characterization of both Ga–H and Ga–C bonds by matrix isolation infrared spectroscopy should be of interest both experimentally and theoretically.

Although the dimer and trimer of gallium have been studied both experimentally[9,10] and theoretically,[11] no information about the reactivities of these clusters has been reported. A study of the reactions of Ga_2 and Ga_3 with molecular hydrogen and methane should provide useful information about species important to mechanisms relating to the growth of Ga-related materials.

We report in this paper the synthesis and characterization of various hydrides for atomic, dimeric, and trimeric gallium. The isolation of $HGaCH_3$ is also described.

Experimental Section

A description of the multisurface matrix isolation apparatus used in this study has been published.[12] In a typical experiment, gallium and hydrogen were cotrapped with Ar or Kr onto a rhodium-coated copper surface over a period of 30 min. Gallium metal was placed in an alumina crucible enclosed in a resistively heated tantalum furnace and vaporized in the temperature range 900–1100 °C. The vaporization temperature was measured with an optical pyrometer. Concentrations of gallium were determined by the temperature of the furnace and also by the quartz crystal microbalance mounted on the matrix block. The amount of H_2 was determined by the rise of the pressure in the chamber. The pressure in the matrix chamber before adding any gases was $\sim 1.0 \times 10^{-7}$ Torr. The IR spectra were recorded using an IBM-98 FT-IR spectrometer with an average of 100 scans and a resolution of 1 cm^{-1}.

The matrix materials, Ar (99.998%, Matheson) and Kr (99.999%, Matheson), were used without further purification. H_2 (99.995%, Matheson), D_2 (99.99%, Air Products), HD (98% isotope, Cambridge Isotope Laboratories), CH_4 (99.97%, Matheson), $^{13}CH_4$ (99.3 atom % ^{13}C, Isotec, Inc.), and CD_4 (99 atom % D, U.S. Services, Inc.) were used as purchased.

Photolysis was performed with a 100-W medium-pressure mercury short arc lamp and long-pass Corning filters after deposition. The photolysis time period was usually 10 min.

Results

I. Reactions of Gallium with Hydrogen. Figure 1 displays the IR spectra for a matrix containing Ga and H_2 in excess Ar, where the ratio of Ga:Ar is ~15:1000 (the temperature of the furnace was ~1100 °C). Five distinct sets of peaks labeled as a–e in Figure 1 have been observed upon cocondensation and after photolysis 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} (set a) and a few weak features between 1900 and 1500 cm^{-1}. The exposure of the matrix surface to light of $\lambda > 520$ nm did not cause any significant changes in the spectrum. Further photolysis with light of 400 nm $< \lambda <$ 520 nm, however, considerably decreased the intensity of set a peaks and enhanced the growth of peaks at 1765.0, 1752.7 and 752.1, 746.8 cm^{-1} (set b) and peaks at 1686.2 and 725.1 cm^{-1} (labeled as c). Subsequent irradiation with UV (320–380 nm) light on the same matrix diminished sets b and c and gave rise to set a peaks again as seen in Figure 1C. Meanwhile, the intensities of peaks d (including two peaks at 1799.0 and 1727.9 cm^{-1}) and peak e (at 1514.1 cm^{-1}) were seen to increase after UV photolysis.

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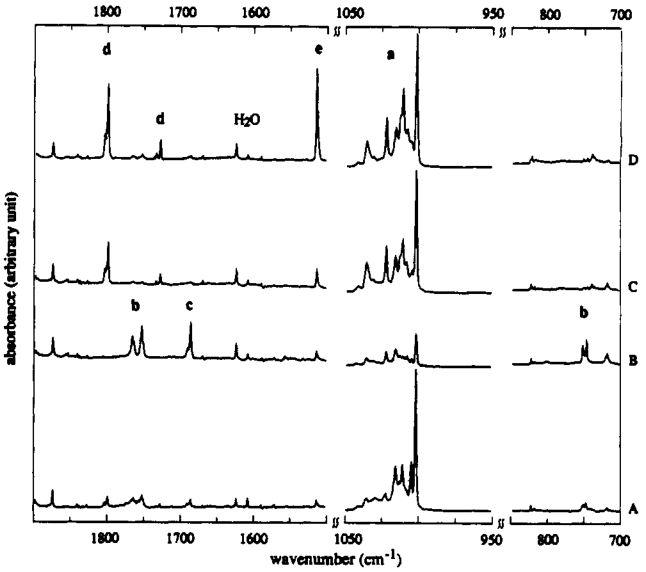

Figure 1. Infrared spectra for a matrix with Ga and H_2 in excess Ar: (A) on deposition; (B) following photolysis with light of 450 nm $< \lambda <$ 520 nm for 10 min; (C) following subsequent photolysis with light of 320 nm $< \lambda <$ 380 nm for 10 min; (D) following subsequent photolysis with light of 270 nm $< \lambda <$ 320 nm for 10 min. a = $Ga_2(b\text{-}H)_2$, b = $Ga_3(t\text{-}H)_2$, c = $Ga_2(t\text{-}H)_2$, d = GaH_2, and e = GaH, where b-H and t-H represent bridging and terminal hydrogens.

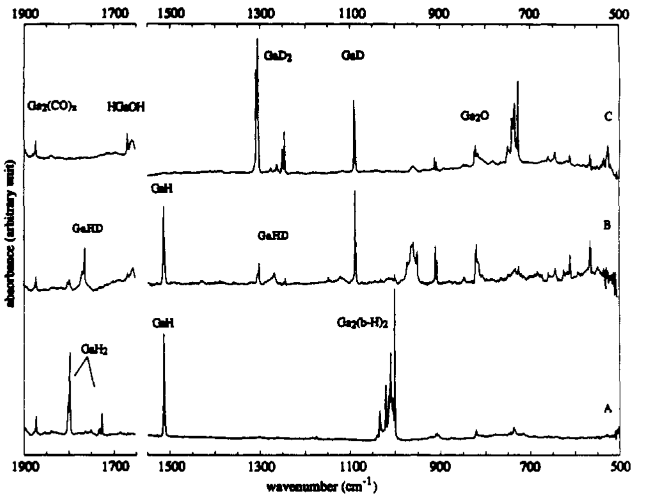

Figure 2. Summary of IR spectra for reactions of gallium with hydrogen in Ar matrices after photolysis with UV (270–380 nm) light: (A) with H_2; (B) with HD; (C) with D_2.

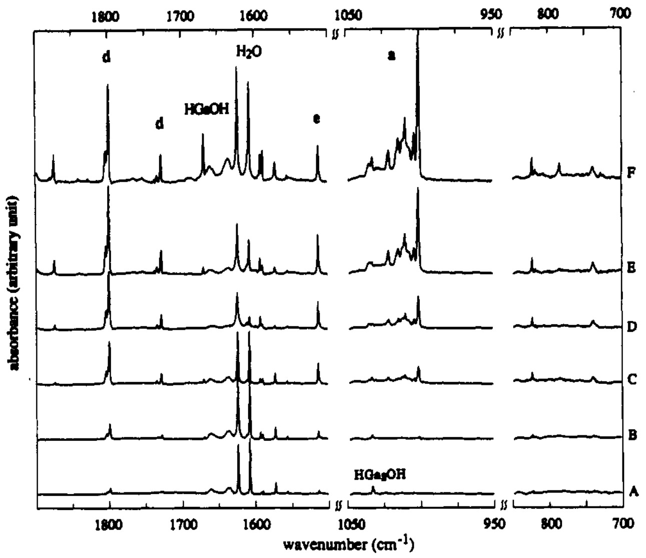

Figure 3. Collection of IR spectra for a series of reactions in Ar matrices with different gallium concentrations (while the pressure of H_2 was kept the same), where spectra were taken after photolysis with UV (270–380 nm) light. Temperatures for vaporization of Ga: (A) 890 °C; (B) 947 °C; (C) 980 °C; (D) 1030 °C; (E) 1060 °C; (F) 1100 °C.

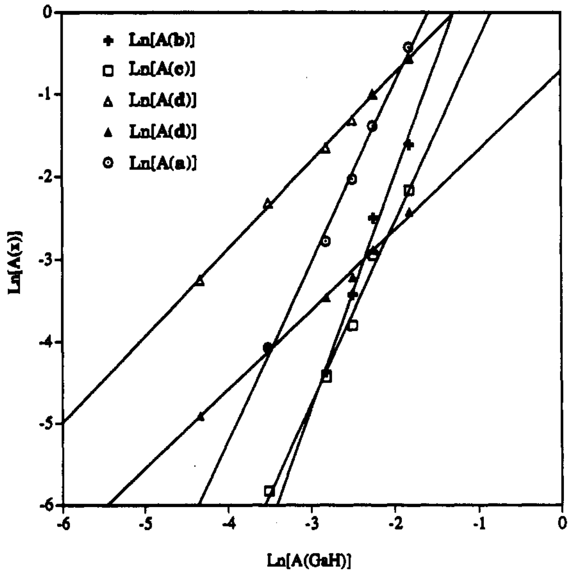

Figure 4. Plot of $\ln[A(x)]$ versus $\mathrm{Ln}[A(\mathrm{GaH})]$. $A(x)$ is the absorbance of band x. a = $Ga_2(b\text{-}H)_2$, b = $Ga_3(t\text{-}H)_2$, c = $Ga_2(t\text{-}H)_2$, d = GaH_2, and e = GaH. The slopes of lines a–d are 2.2, 2.9, 2.2, and 1.1(ν_1), 1.0(ν_3), respectively.

Figure 2 shows a collection of IR spectra for reactions of gallium with H_2, HD, and D_2 after the respective matrices were photolyzed with UV (280–370 nm) light. All the peaks mentioned above showed a large isotopic shift when D_2 was employed. This clearly indicates that all peaks are due to Ga–H vibrations. As noticed in Figure 2B, in the reactions of Ga with HD the spectrum was complicated by the coexistence of Ga–H and Ga–D vibrations. Nevertheless, peaks e also appear 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 H_2 and D_2, respectively. From the Ga concentration studies described later, we conclude that only one Ga atom is involved in this molecule, and we assign this as gallium monohydride, GaH. The vibrational frequency of GaH in the gas phase[13] was observed to be 1546.9 cm^{-1}, which suggests that GaH has a moderate gas-matrix shift ($\sim$32 cm^{-1}).

A summary of IR spectra from a Ga concentration study is illustrated in Figure 3, where the amount of added H_2 was kept constant (2.0 × 10^{-6} Torr) and the concentration of Ga was increased gradually. It is obvious that as the concentration of Ga increases, the intensities of peaks d (GaH_2) and e (GaH) rise steadily, while absorptions a–c seem to be predominantly present under higher gallium concentrations. The ln–ln plots[14] of the intensities of bands corresponding to each species versus the absorption of GaH are shown in Figure 4, 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 peaks. The use of the ln–ln plots in the analysis of concentration-dependent data derived from matrix isolation studies is based on the assumption that the formation of a complex formed from two species reacting on the matrix surface obeys a simple mass-action law. Thus the rate of formation of the complex is proportional

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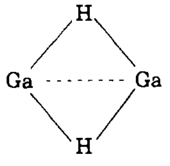
to the product of the flux of the two species, and the order of the metal dependence can be considered without concern for the actual rate. It should be noted that the use of this plot does not imply that all the metal has reacted or that one achieves a state of equilibrium.

It is suggested from the slopes (2.2, 2.9, 2.2, and 1.1 for peaks a–d, respectively) that species d results from atomic Ga reactions and both species a and c are due to diatomic Ga_2 reactions, while band b may arise from a triatomic Ga_3 reaction product.

The d peaks shifted to 1303.4 and 1245.1 cm^{-1} in D_2 reactions and exhibited 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. The fact that in an 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 strongly indicates that species responsible for set d peaks can be assigned as gallium dihydride, GaH_2. The peaks at 1799.0 and 1727.9 cm^{-1} are thus assigned to the antisymmetric stretching (ν_3) and the symmetric stretching (ν_1) mode for GaH_2. A shoulder on each of these peaks was observed, and this is thought to be due to different matrix sites because similar splitting is also observed for those peaks in HD and D_2 reactions. From the known optical spectra,[15] Ga was excited from the ^2P state to a ^2D 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.

As discussed above, the peaks labeled as a can be assigned to a species involving two Ga atoms. In a previous report[16] on reactions of gallium with water, these peaks were assigned to $Ga_2H(OH)$ with both bridging H and OH groups. However, from this study, only one peak at 1030 cm^{-1} seems to have a correlation with the H_2O concentration, as indicated in Figure 3. The peaks at 1002.1 and 1015.8 cm^{-1} show a large shift in D_2 reactions and exhibit two sets of peaks with one in the Ga–H region and one in the Ga–D region in those reactions with HD. Thus we reassigned species a as Ga_2H_2 with two bridging hydrogens and no terminal hydrogens, since no IR peaks in the terminal hydrogen region were seen in association with it. Species a is thought to have the following structure:



a

where some bonding may exist directly between gallium atoms. The appearance of these peaks in the previous study may have resulted from the reactions of Ga_2 with a small amount of impurity H_2 which was always present in the vacuum chamber.[17] The observed frequencies and their tentative assignments are listed in Table I.

As pointed out earlier, species c is also related to the dimer of gallium, Ga_2. This set of peaks 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. In addition, this species is thought to involve only one H_2 molecule because the intensities of the 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 assumed with the following structure:

Table I. Observed Frequencies (cm^{-1}) for Ga_xH_y

	GaH_2		GaD_2			GaHD	
	Kr	Ar	Kr	Ar		Kr	Ar
asym str	1796.4	1799.1 (0.57)[a]	1302.4 (0.66)	1303.4	Ga–H	1763.6	1766.2
sym str	1730.8	1727.9 (0.09)	1244.2 (0.11)	1245.1	Ga–D	1261.2	1269.6

GaH		GaD	
1507.6	1514.1	1086.5	1090.3

Ga_3H_2		Ga_3D_2			Ga_3HD	
Kr	Ar	Kr	Ar		Kr	Ar
1740.4	1752.8	1253.3	1262.9	Ga–H	1746.2	1759.0
1753.2	1765.8	1267.2	1276.2	Ga–D	1260.5	1262.9

	Ga_2(b-H)$_2$		Ga_2(b-D)$_2$		Ga_2(b-HD)	
Ga–H str	1022.3	1002.1[b]			953.1	952.7
Ga–D str			743.0	728.2	*c*	728.5

	Ga_2(t-H)$_2$		Ga_2(t-D)$_2$		Ga_2(t-HD)	
Ga–H str	*c*	1686.2			*c*	1685.9
Ga–D str			1218.2	1206.5	1219.0	1206.5

[a] The numbers in parentheses provide a relative measurement of the intensities of two stretching modes. [b] Indicates the strongest peak in the band. [c] Indicates that the peak is too weak to observe.

H —— Ga -------- Ga —— H

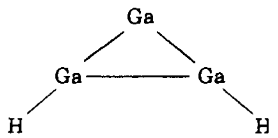
c

where the Ga–Ga interaction may contain some double-bond character. However, whether the molecule is linear is not certain. As shown in Figure 1, bands a and c can be photolytically converted to each other according to the following reaction:

$$\underset{\mathbf{a}}{Ga_2(b\text{-}H)_2} \underset{320\text{-}380\ nm}{\overset{400\text{-}520\ nm}{\rightleftarrows}} \underset{\mathbf{c}}{Ga_2(t\text{-}H)_2}$$

The ability to convert the two species reversibly supports the assignment to Ga_2 species with either bridging or terminal hydrogens.

Peaks labeled as b shift to 1262.9 and 1276.2 cm^{-1} in a D_2 reaction. In an HD reaction, only two peaks were observed, one 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. It is also noted that the two observed Ga–H stretching modes are separated by only 13 cm^{-1}, which is much smaller than the separation for GaH_2 (72 cm^{-1}). This suggests that the interaction between the two Ga–H vibrations of this species 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_3H_2, with the following geometry is tentatively assigned:



b

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Table II. Reaction Product Absorptions (cm^{-1}) for Reactions of Gallium with Hydrogen in Ar and Kr Matrices

obs freq (cm^{-1})			
Ar	Kr	assignt	label
1874.0	1872.5	$Ga_2(CO)_x$	
1799.0, 1727.9	1796.4, 1730.8	GaH_2	d
1766.2, 1269.6	1763.6, 1261.2	GaHD	d
1670.0	1665.0	H–GaOH	
1575.0	1570.5	$Ga(OH_2)$	
1514.1	1507.6	GaH	e
1686.2		$Ga_2(t\text{-}H)_2$	c
1685.9, 1206.5		$Ga_2(t\text{-}HD)$	c
1752.8, 1765.8	1740.4, 1753.2	$Ga_3(t\text{-}H)_2$	b
1759.0, 1262.9	1746.2, 1260.5	$Ga_3(t\text{-}HD)$	b
1262.9, 1276.2	1253.3, 1267.2	$Ga_3(t\text{-}D)_2$	b
1303.4, 1245.1	1302.4, 1244.0	GaD_2	d
1206.5	1218.2	$Ga_2(t\text{-}D)_2$	c
1090.3	1086.5	GaD	e
1002.1	1022.3	$Ga_2(b\text{-}H)_2$	a
822.4	815.5	Ga_2O	
728.2	704.6	$Ga_2(b\text{-}D)_2$	a
952.7, 680.1	953.1, 655.0	$Ga_2(b\text{-}HD)$	a

In this case, the 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 related to 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. Balasubramanian et al.[11] have computed that the ground state of Ga_3 is a $^2A_1$ state with an equilibrium geometry of a near-equilateral triangle, which also supports our assignment.

As seen in Figure 2, 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 probably results from reactions of Ga_2 with CO to give $Ga_2(CO)$, where CO comes from the degassing of the cell and the gallium sample. We also noted that the peak at 822.1 cm^{-1} is not related to H_2 either, since it has previously been assigned to Ga_2O.[18] This species most likely results from a certain amount of oxide in the gallium sample.

The reactions between Ga and H_2, D_2, and HD have been studied in Kr matrices as well. 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 Ga_3H_2, $Ga_2(t\text{-}H)_2$, and $Ga_2(b\text{-}H)_2$ can be found in Tables I and II. Surprisingly, UV photolysis (280–320 and 320–380 nm), which usually produced GaH_2 in Ar matrices, did not yield the intense peaks which can be assigned to the stretching modes for GaH_2. Only GaH (at 1507.6 cm^{-1}) was seen to grow dramatically after UV photolysis. This peak is observed to shift to 1086.5 cm^{-1} for GaD. Also, although the intensity for GaH is higher than that for GaH_2, it is still much smaller than that in an Ar matrix. The formation of lesser amounts of gallium–hydrogen products is thought to be due to the possibility that krypton binds more strongly with Ga than does argon, thus inhibiting the formation of the hydrogen complex.

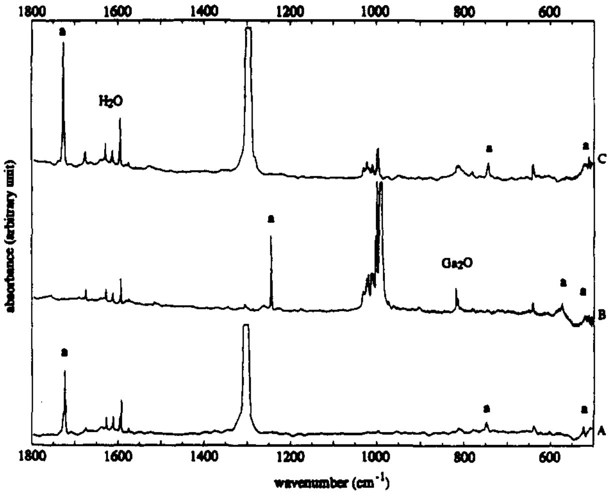

Figure 5. Summary of IR spectra for reactions of gallium with methane in Ar matrices after UV (270–380 nm) photolysis: (A) with CH_4; (B) with CD_4; (C) with $^{13}CH_4$. a = methylgallium hydride.

Table III. Infrared Frequencies (cm^{-1}) for Methylgallium Hydride in Ar, Kr, and Methane Matrices

	Ar	Kr	methane
$H\text{–}GaCH_3$	1719.7	1712.5	1709.6
$H\text{–}Ga^{13}CH_3$	1719.7	1712.7	1705.7
$D\text{–}GaCD_3$	1243.6	1239.0	1285.8
$HGa\text{–}CH_3$	528.6	520.0	524.0
$HGa\text{–}^{13}CH_3$	515.4	*a*	519.2
$DGa\text{–}CD_3$	525.0	*a*	*a*
$\rho(CH_3)$	753.1	747.8	768.9
$\rho(^{13}CH_3)$	748.7	746.8	745.3
$\rho(CD_3)$	578.2	*a*	589.8
$\delta(CH_3)$	1176.4	1153.7	1153.7
$\delta(^{13}CH_3)$	*a*	1153.5	1146.0
$\delta(CD_3)$	*a*	747.0	786.0

[a] Indicates band too weak to observe or obscured by strong parent methane absorptions.

II. Reactions of Gallium with Methane. Figure 5 shows a collection of the IR spectra for the photoreactions of Ga with CH_4, CD_4, and $^{13}CH_4$ in Ar matrices. 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 occurs at 1719.7 cm^{-1} and exhibits a large shift in CD_4 reactions and almost no change in $^{13}CH_4$ reactions, as illustrated in Figure 5. We conclude that this peak results from the insertion of Ga into an H–C bond in CH_4. We also noticed that this peak is readily removed when the same matrix surface is photolyzed with light of $\lambda > 580$ nm. A decomposition product is not observed; however, it was reported[19] in studies of reactions of Al with CH_4 that $HAlCH_3$ reverts to Al and CH_4. A similar reaction is also expected for $HGaCH_3$. A gallium and methane concentration study revealed that this species only involves one Ga atom and one CH_4 molecule. We thus assign the observed peak to $HGaCH_3$. A second absorption observed at 528.6 cm^{-1} for the CH_4 reaction shifts to 515.0 cm^{-1} for a $^{13}CH_4$ reaction but undergoes only a small shift for a CD_4 reaction. This peak is thought to be due to the Ga–C stretching mode. It is also noted that a peak at 754.3 cm^{-1} in a CH_4 reaction shifts slightly to 748.7 cm^{-1} in a $^{13}CH_4$ reaction and undergoes a large shift to 578.3 cm^{-1} in a CD_4 reaction. These peaks have been assigned to a methyl rocking mode, $\rho(CH_3)$. Several other anticipated C–H stretching and angle deformation modes of CH_3 for methylgallium hydride either were too weak to observe or obscured by strong absorptions of parent CH_4, as noted in Table III. Unlike the studies of the reactions with H_2, the concentration studies indicated that no reactions between small clusters, such as Ga_2, Ga_3, and CH_4, were observed. A series of reactions with different concentrations of CH_4 have also been carried out in Ar matrices; no reactions due to more than one CH_4 molecule were observed.

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 III. The relative intensities of the assigned modes seem to be matrix dependent presumably because of the different interactions of methylgallium hydride, CH_3GaH, with the matrix materials.

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Table IV. Comparisons of Terminal H–Ga Bonds among Observed Species in Ar Matrices

	ω (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	k_{Ga-H} (mdyn/Å)
H–Ga[a] (gas)	1546.9	1604.5	28.8	1.51
H–Ga	1514.1	1570.9	28.4	1.44
H–GaD	1766.2	1823.0	28.9	1.95
H–GaOH[b]	1669.8	1791.5	60.9	1.89
H–$GaCH_3$	1719.7	1818.6	49.4	1.94
H–Ga_2H_5[c]	1985, 2015	2039, 2069	~27.0	2.47

[a] From ref 13. [b] From ref 16. [c] From ref 5.

Discussion

It is of interest to compare the frequencies and force constants of gallium hydride species observed in this study to those of species which have been previously studied. Table IV lists some known species with terminal Ga–H bonds and their vibration frequencies. The approximate stretching force constants for the Ga–H stretching mode have been calculated with a diatomic approximation and vibrational frequencies for the H–Ga and D–Ga stretching modes, using the following equations:[20]

$$\omega_e{}^D = \rho\omega_e{}^H, \qquad \omega_e{}^D x_e{}^D = \rho^2\omega_e{}^H x_e{}^H \tag{1}$$

$$\omega^i = \omega_e{}^i - 2\omega_e{}^i x^i, \qquad \rho = [\mu^H/\mu^D]^{1/2} \tag{2}$$

where ω^i are the observed frequencies, μ^i are the reduced masses, and $x_e{}^i$ are the anharmonicities. The resulting values are given in Table IV.

One notices immediately the general increase in frequency and force constant for the hydride bond of the divalent species as compared to the case for the monohydride (GaH). Bonding in the monohydride occurs largely through the 4p orbital of gallium with the ground-state s^2p configuration. The dihydride necessarily requires involvement of the sp^2 excited-state configuration. The increased involvement of s orbital character is consistent with a higher bond force constant and a higher frequency for the dihydride. It is also interesting to find that HGaOH has a lower frequency and a lower force constant for the Ga–H bond relative to those of GaH_2. Typically as found for transition metals, a strongly withdrawing group is expected to increase the effective nuclear charge on the metal, which results in a contraction of the bonding orbitals and thus an increase in the stretching frequency and force constant.[21] This expected effect for HGaOH is apparently overwhelmed by a change in electronic structure which results in a weakening and an increased anharmonic character in the hydride bond.

The bond angles for species such as Ga_3H_2, $Ga_2(b\text{-}H)_2$, and $Ga_2(t\text{-}H)_2$ cannot be determined from the limited information obtained in this study. Further understanding of the molecules will benefit greatly from quantum mechanical calculations. The bond angle for GaH_2, 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 GaH_2 which were obtained from integration of peak areas are listed in Table I together with the frequencies. The bond angle is obtained by using the following relationship:[22]

$$\frac{I_{B_2}}{I_{A_1}} = (\tan^2\theta)\frac{m_M + 2m_H\sin^2\theta}{m_M + 2m_H\cos^2\theta} \tag{3}$$

where m_M and m_H are the masses of the metal and hydrogen, I_{B_2} and I_{A_1} are the relative intensities of the antisymmetric and symmetric stretching modes, and 2θ is the apical angle. A result of 136° for 2θ is obtained in an Ar matrix using the relative intensities for GaH_2. For GaD_2, the bond angle is calculated to be 135°. No attempt was made to determine the bond angle for GaH_2 in a Kr matrix because the peaks were too weak to be measured accurately. The uncertainties in measurements of peak intensities and the effects of assumptions made are believed to be small, and an upper limit of ±5° error in the bond angle measurement is suggested. A bond angle of 136° suggests partial sp and sp^2 bonding in GaH_2.

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.

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