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Matrix Infrared Spectra of Aluminum, Gallium, and Indium Complexes with Acetylene

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Aluminum, gallium, and indium atoms have been codeposited from thermal sources with C_2H_2 at high dilution in argon on a 12±1 K CsI window. The major products are best characterized as 1/1 π complexes where the metal shares electron density from one acetylene π orbital. Higher reagent concentrations give evidence for 1/2 and 2/1 metal–acetylene complexes. In the case of aluminum, photolysis induces insertion to form $HAlC_2H$ and AlC_2H.

Introduction

Reaction products of metal atoms and hydrocarbon molecules are important for understanding chemisorption and catalytic processes. Aluminum adducts with acetylene have been examined by ab initio calculations, and a number of stable Al–C_2H_2 isomers have been predicted.[1-5] Figure 1 shows the isomeric forms of Al–C_2H_2 that are calculated to be stable; the vinylidene $AlCCH_2$ (**1**) and the insertion product HAlCCH (**2**) structures vie for the global minimum in energy.[3] The next most stable are the three-membered Al–C_2 ring, structure **3**, and the Dewar–Chatt–Duncanson π complex **4**, which are followed by the σ-bonded substituted vinyl radicals with H atoms cis or trans as in **5** or **6**, respectively. These last two structures were identified as the primary Al–C_2H_2 species in matrix isolation ESR experiments, which reported that the cis isomer formed on deposition was converted to the trans isomer on irradiation with UV–vis light.[6,7] The ab initio SCF calculations also predict that the π-bonded structure **4** is a transition state between the cis **5** and trans **6** structures.[3] However, when electron correlation effects were included, the π-bonded structure **4** became more stable by 2 kcal/mol than the trans structure **6**, and the cis structure **5** was not even a stable local minimum.[3,4]

In the related Al–C_2H_4 system, Manceron and Andrews[8] assigned the argon matrix IR spectra to a π-bonded Al–C_2H_4 complex. This Al–C_2H_4 complex was first characterized by Kasai and McLeod[7,9] in matrix isolation ESR experiments and has subsequently[10,11] been found to be stable in adamantane matrices up to 297 K. Ab initio calculations[1,12] have determined dissociation energies for both the Al–C_2H_2 and the analogous Al–C_2H_4 π complexes and found that the Al–C_2H_2 complex **4** was more stable by 6.9 kcal/mol. It is therefore difficult to reconcile the ESR observation of σ-bonded structures **5** and **6** with the apparent stability of the π-complex structure **4** and stable π-bonded Al–C_2H_4 complex.

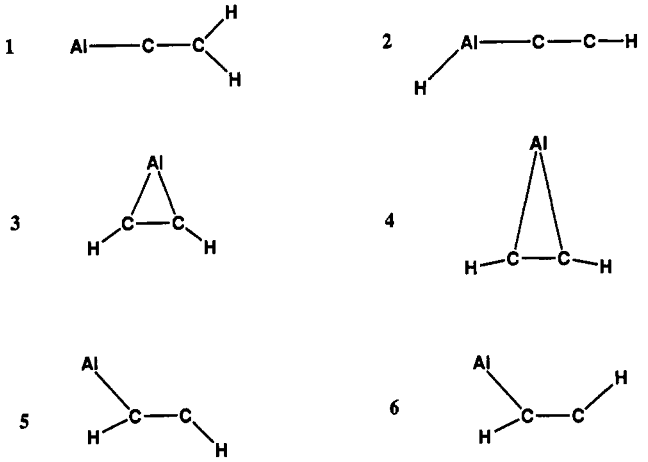

Figure 1. Stable isomers calculated for AlC_2H_2 species.[3]

A number of other metal atom reactions with acetylene have been studied. The metals Li, Cu, Ag, and Au all form π complexes, but Fe inserts into a C–H bond.[13-16] Very recent boron atom reactions with acetylene give the three-membered-ring BC_2H_2 and the HBC_2H insertion species predicted to be stable products.[5,17] It will be interesting to characterize bonding in the MC_2H_2 systems for the group 13 atoms.

Experimental Section

The experimental techniques of matrix isolation spectroscopy have been described previously in some detail.[18-20] High-purity acetylene (Matheson), argon (99.995%, Air Products),[13] and C_2H_2 (90% ^{13}C) and C_2D_2 (98% D) (Merck Sharp and Dohme) were all used without further purification. Al (99.998%, Aesar), Ga (99.99999%, Aesar), and In (99.99%, Indium Corp. of America) metals were outgassed at operational temperatures (1300, 1100, and 900 °C, respectively) for several hours before deposition. Gas mixtures varied in concentration from M/R (Ar/C_2H_2) of 200/1 to M/R of 800/1 and were deposited on the 12 K window at about 3 mmol/h for 8–20 h. Ga and In were heated in graphite crucibles with 0.020-in. W wire while Al samples were heated directly on a small 0.030-in. W wire basket. Metal deposition rates were monitored by a quartz crystal microbalance mounted in close proximity to the cold window. Metals were deposited at rates of 0.5–2 μmol/h to achieve metal/acetylene

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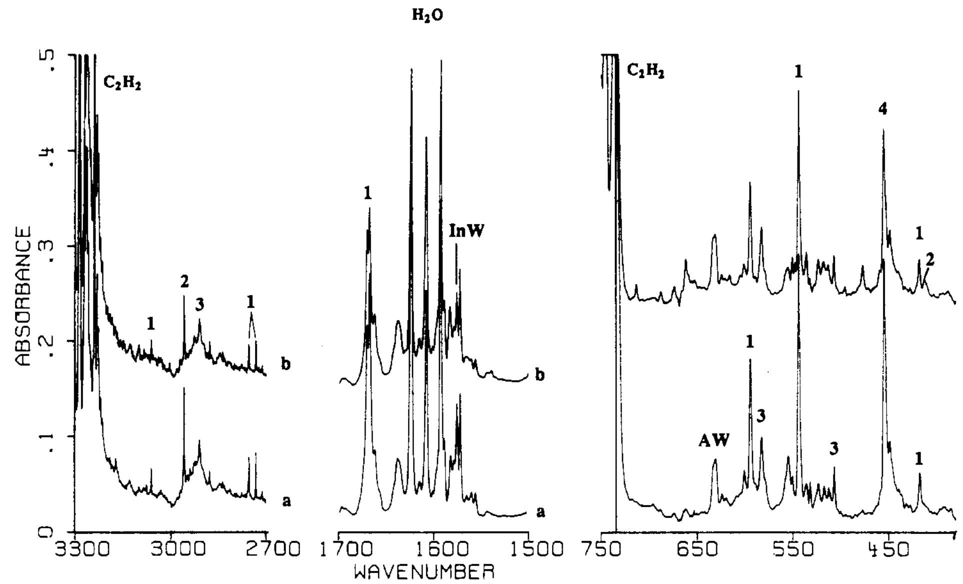

Figure 2. Infrared spectra of C_2H_2 codeposited with in atoms in an Ar matrix (Ar/C_2H_2 = 400/1): (a) on deposition; (b) after annealing to 35 K. InW denotes indium–water complex; AW denotes C_2H_2--H_2O complex.

Table I. Observed Product Bands for Indium Codeposited with C_2H_2 in an Argon Matrix

C_2H_2	$^{13}C_2H_2$	C_2D_2	mode	group
3062	3043	2312	ν(CH)	1
2755	2746			
2733	2723			
1668	1611	1547	ν(CC)	
595.0	591.0	436.0	δ(CCH)	
544.0	542.0	409.0	δ(CCH)	
418.0	404.0	387.0	ν(InC)	
2960	2947	2217	ν(CH)	2
411.5				
2879	2871	2194	ν(CH)	3
583.0	580.0	435.0	δ(CCH)	
507.0	504.0		δ(CCH)	
455.0	441.0	428.0	ν(InC)	4
354.0	343.0	323.0	ν(InC)	

ratios in the 1/100 to 1/15 range. UV–vis irradiation was accomplished by focusing the full light ($\lambda > 254$ nm) of a 175-W medium-pressure Hg arc lamp through a quartz lens onto a 12-mm Suprasil beam pipe for 1-h periods. The matrix was warmed to 25–35 K by a resistance heater mounted on the window holder. Spectra were recorded on a Nicolet 5-DXB FTIR with 2-cm^{-1} resolution. Final spectra are averages of 2000–4000 scans with wavenumber accuracies of ±0.5 cm^{-1}.

Results

Infrared spectra will be presented for matrix reactions of acetylene with the group 13 metal atoms In, Ga, and Al in turn.

Indium. Figure 2 shows spectra obtained upon deposition of indium atoms with Ar/C_2H_2. Bands for H_2O, CO_2, CO, CH_4, and isolated and aggregated C_2H_2 and for the C_2H_2--H_2O, In--H_2O, and In--CO complexes were observed.[21,22] In addition to all of these bands, new bands appeared corresponding to products of the reaction of In with acetylene, which are listed in Table I.

Product bands are grouped by absorbance behaviors on deposition, with respect to variations of acetylene and indium concentrations, and upon annealing of the matrix. These groupings were also applied to the observed $^{13}C_2H_2$ and C_2D_2 spectra in order to discern the isotopic counterparts of the product bands. The bands assigned to group 1 species are present in all of the experiments and are persistent, even at low In and C_2H_2 concentrations. Group 1 absorptions decreased in intensity upon annealing of the matrix. The bands assigned to group 2 are present on deposition only in more concentrated acetylene matrices and show little dependence on In concentration. Group 2 species appeared in 800/1 matrices only after annealing, suggesting that more than one C_2H_2 molecule is involved. Group 3 and group 4 species are both present in matrices with low In/C_2H_2 ratios, but the group 4 species bands are more sensitive to the In concentration. Specifically, the group 3 species bands are present in larger In/C_2H_2 ratio samples after annealing while group 4 species bands are not. When both sets of bands are present, they display different annealing behaviors; the group 3 bands increase in intensity while the group 4 bands decrease.

Isotopic substitutions were made in order to identify the types of vibrations associated with each group. In the low-frequency region, the two group 1 bands at 595.0 and 544.0 cm^{-1} show slightly different H/D ratios, 1.364 and 1.328, respectively, but very small $^{12}C/^{13}C$ shifts indicative of CCH bending motions. The 418.0-cm^{-1} band, however, shows a very large $^{12}C/^{13}C$ ratio of 1.0336 and a small H/D ratio of 1.0798, which is expected for an In–C stretching motion. In the C–H stretching region, the group 1 species shows an intense band at 3062 cm^{-1} which behaves in the same manner as a pair of bands at 2755 and 2733 cm^{-1} upon annealing. The 3062-cm^{-1} band shows an H/D ratio of 1.325 and a small $^{12}C/^{13}C$ ratio of 1.0064. Unfortunately, the C_2D_2 counterpart to the 2755/2733 cm^{-1} pair was not observed, but the bands show identical ^{13}C shifts of 9 cm^{-1} and the spacing is the same (22 cm^{-1}) in both isotopic experiments. The group 1 band at 1668 cm^{-1} shifts more on deuterium (1547 cm^{-1}) than on ^{13}C substitution (1611 cm^{-1}), as seen in Figure 3, indicating strong coupling to a C–H mode. This is also indicated by the large ^{13}C shift of the 3062-cm^{-1} band (19 cm^{-1}) relative to that of the 2755/2732 cm^{-1} bands (9 cm^{-1}).

The group 2 band at 411.5 cm^{-1} has no observable $^{13}C_2H_2$ or C_2D_2 counterparts. The band at 2960 cm^{-1} shows a small $^{12}C/^{13}C$ ratio of 1.0045 and a large H/D ratio of 1.3352. The group 3 bands at 583.0 and 507.0 cm^{-1} have small $^{12}C/^{13}C$ ratios of 1.0048 and 1.0058, respectively, and the 583.0-cm^{-1} band has a large H/D ratio of 1.341. These are consistent with CCH bending motions. However, the group 4 bands at 455.0 and 354.0 cm^{-1} show large $^{12}C/^{13}C$ ratios of 1.0318 and 1.0317, respectively, and relatively small H/D ratios of 1.0636 and 1.0943, which implies that these are M–C motions. The band at 2879 cm^{-1}, tentatively assigned to group 3, although it could also be assigned to group

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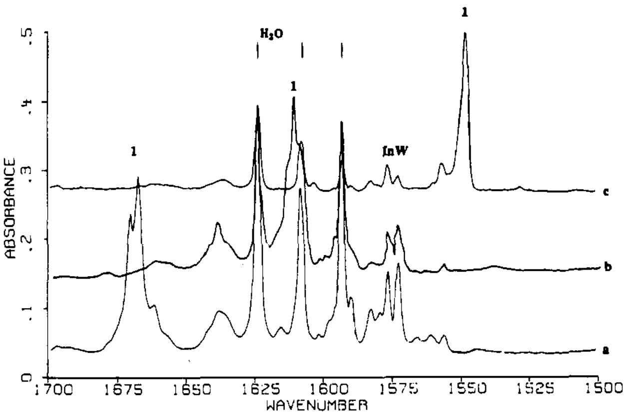

Figure 3. Infrared spectra of argon, acetylene, and indium atom samples in the 1700–1500-cm^{-1} region (Ar/C_2H_2 = 400/1): (a) C_2H_2; (b) $^{13}C_2H_2$; (c) C_2D_2.

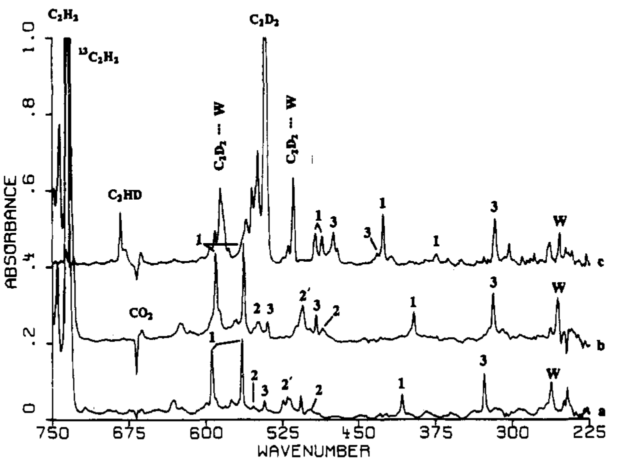

Figure 4. Infrared spectra of argon, acetylene, and gallium atom samples in the 750–225-cm^{-1} region (Ar/C_2H_2 = 400/1): (a) C_2H_2; (b) $^{13}C_2H_2$; (c) C_2D_2.

4, shows a very small $^{12}C/^{13}C$ ratio of 1.0028 but a large H/D ratio of 1.3122.

Gallium. Observed bands were grouped according to behavior on deposition, with respect to concentration changes, and upon annealing of the matrices at 25 and at 35 K. An attempt was made to remain consistent with the groupings used for indium. Figure 4 shows a typical spectrum obtained upon deposition of Ga atoms with C_2H_2, and the product absorptions are listed in Table II.

The prominent bands assigned to the group 1 species at 2992, 2768, 1682, 595.0, 566.0, and 408.0 cm^{-1} are present on deposition for all observed concentrations of Ga and C_2H_2. These absorptions decrease upon annealing at 25 K, and at 35 K the bands all but disappear. The rather broad absorptions corresponding to group 2 species are present on deposition in only the most concentrated C_2H_2 experiments. These bands grow slightly on annealing at 25 K and grow even more on annealing at 35 K in all of the observed spectra. The broad absorptions at 525.0, 521.0, and 518.0 cm^{-1} of group 2′ are present in all spectra on deposition and increase in intensity after annealing at both 25 and 35 K. There seems to be a slight dependence on C_2H_2 concentration, but the observed bands do not correlate with the group 2 bands which are not present on deposition in low C_2H_2 concentration matrices. The bands assigned to the group 3 species are small, sharp absorptions which are present on deposition in all of the observed spectra and which increase in intensity after annealing at 25 K but decrease slightly after annealing at 35 K. Group 3 bands are dependent on Ga concentration; the intensity of these bands on deposition relative to those of group 1 increases with increasing Ga concentration.

Table II. Observed Product Bands for Gallium Codeposited with C_2H_2 in an Ar Matrix

C_2H_2	$^{13}C_2H_2$	C_2D_2	mode	group
2292	2981	2242	ν(CH)	1
2768	2755			
1682	1624	1563	ν(CC)	
595.0	591.0	486.0	δ(CCH)	
566.0	563.0	426.0	δ(CCH)	
408.0	396.0	375.0	ν(GaC)	
2973	2959		ν(CH)	2
1680		1559	ν(CC)	
555.0	551.0	480.0	δ(CCH)	
551.0	549.0		δ(CCH)	
500.0	486.0		ν(GaC)	
318.0	310.0	310.0	ν(GaC)	
2936	2925		ν(CH)	2′
525.0	512.0	491.0	ν(GaC)	
518 (site)	506 (site)			
412.0	402.0	363	ν(GaC)	
544.0	541.0	431	δ(CCH)	3
507.0	492.0	475.0	ν(GaC)	
328.0	319.0	317.0	ν(GaC)	

Isotopic substitution reveals that the most prominent group 1 bands in the low-frequency region, at 595.0 and 566.0 cm^{-1}, have large H/D ratios of 1.224 and 1.327, respectively, and very small ^{13}C shifts indicative of CCH bending motions. The 408.0-cm^{-1} band, however, shows a $^{12}C/^{13}C$ ratio of 1.030 and a H/D ratio of 1.089, which is characteristic of a Ga–C stretch. In the C–H stretching region the 2992.0-cm^{-1} band shows an H/D ratio of 1.334 and a small $^{12}C/^{13}C$ ratio of 1.0037. This band correlates with the annealing behavior of the band at 2768.0 cm^{-1}, which shows a small ^{13}C shift, but there is no corresponding band observed for C_2D_2. The band at 1682 cm^{-1} in the C–C stretching region shifts on ^{13}C substitution to 1624.0 cm^{-1}, but even more on deuterium substitution, to 1563 cm^{-1}, suggesting coupling with a C–H stretching mode.

The group 2 bands at 555.0 and 551.0 cm^{-1} shift slightly different amounts with ^{13}C substitution, 4.0 and 2.5 cm^{-1}, respectively, but only one D counterpart is observed. Surprisingly, this species displays two Ga–C stretches at 500.0 and 318.0 cm^{-1}. These two bands display ^{13}C shifts of 14.7 and 8.0 cm^{-1}, respectively, but only one D counterpart was observed at 310.0 cm^{-1}. The bands in the C≡C stretching region which correlate with this species are shifted slightly to the red of the group 1 species bands by 2.7 and 3.1 cm^{-1} in the H and D experiments, respectively. The band in the C–H stretching region is a broad absorption at 2973 cm^{-1} showing a 13.0-cm^{-1} ^{13}C shift and no D counterpart, suggesting some mixing with the C–C stretching mode.

The group 2′ species also seems to have two Ga–C stretches with the 525.0-cm^{-1} band shifting 12.5 cm^{-1} and the 412.0-cm^{-1} band shifting 9.7 cm^{-1} with ^{13}C substitution. The broad band in the C–H stretching region at 2936 cm^{-1} shows a 10.8-cm^{-1} ^{13}C shift.

The sharp group 3 band at 544.0 cm^{-1} shows a small ^{13}C shift and an H/D ratio of 1.259, indicating a CCH bending mode. The band at 507.0 cm^{-1} shows a ^{13}C shift of 14.9 cm^{-1} and a small D shift of only 32.6 cm^{-1}, and the 328.0-cm^{-1} band also shows a significant ^{13}C shift to 319.0 cm^{-1} and a relatively small D shift to 317.0 cm^{-1}; this evidence identifies a Ga–C stretching mode.

Aluminum. The aluminum experiments gave weak aluminum oxide[23] and carbonyl[24] bands and the only products susceptible to change upon irradiation with UV light (λ > 254 nm). There were enough similarities, however, to maintain some consistency with the groupings used for Ga and In. Table III shows the results for Al codeposited with acetylene. There were no bands

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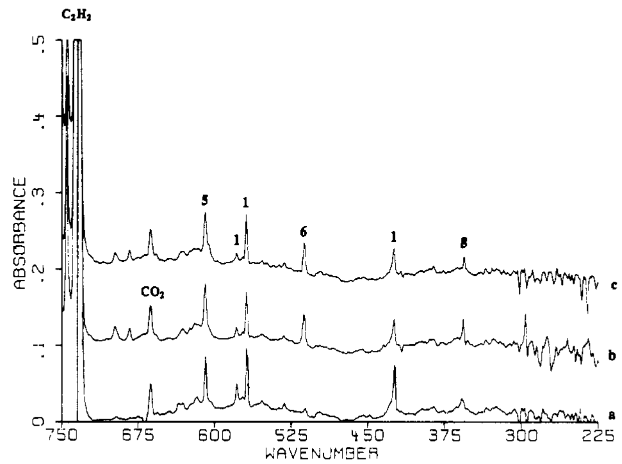

Figure 5. Infrared spectra of argon, acetylene, and aluminum atom samples in the 750–225-cm^{-1} region (Ar/C_2H_2 = 400/1): (a) on deposition; (b) after final irradiation with medium-pressure Hg arc lamp ($\lambda > 254$ nm) for two 1-h periods; (c) after annealing to 35 K.

Table III. Observed Product Bands for Aluminum Codeposited with C_2H_2 in an Argon Matrix

C_2H_2	$^{13}C_2H_2$	C_2D_2	mode	group
569.0	566.4	429.7	$\delta(CCH)$	1
579 (site)	576 (site)	435 (site)		
424.8	417.0	405.8	$\nu(AlC)$	
609.0	605.6		$\delta(CCH)$	5
618 (site)	615 (site)			
1976.4	1905.8	1860.8	$\nu(CC)$	6
512.8	501.9	456.0	$\nu(AlC)$	
683.5	676.6	505.2	$\delta(HCC)$	
2000.8	1929.2	1882.7	$\nu(CC)$	7
1804.1	1804.1	1314.8	$\nu(AlH)$	
358	353		$\nu(AlC)$	8

observed in the C–H bending region, and as seen in Figure 5, the absorptions are weak compared to the Ga and In cases. Furthermore, no bands particularly sensitive to Al concentration were observed; Al is more difficult to evaporate, and the Al concentration in these experiments is less than the Ga and In concentrations employed here.

Group 1 bands at 569 and 425 cm^{-1} are present upon deposition through all experimental concentration changes and decrease 10% in intensity upon each of two successive irradiations with UV light. Furthermore, the group 1 band intensities decrease slightly upon annealing of the matrix, which is consistent with the annealing behavior displayed by group 1 species for In and Ga. Group 5 bands are also present in the matrix initially and are as intense as the group 1 bands in some experiments, but in contrast to the group 1 bands, they increase 15% on the first irradiation (and decrease 15% on the second irradiation). There is no obvious Al concentration dependence, so the species probably has the 1/1 stoichiometry of group **1**.

A new group of bands, labeled **6**, is very weak upon deposition but grows dramatically upon irradiation with UV light (512.8 and 1976.4 cm^{-1} (A = 0.015 not shown)) and increases by 50% in the second hour of photolysis. Bands at 2000.8 and 1804.1 cm^{-1} (group 7, not shown) are produced in the first photolysis (A = 0.01 and 0.03, respectively) and are reduced by 20% in the second photolysis. Finally, the band labeled 8 at 358 cm^{-1} is produced on deposition and increases 30% in each photolysis. This is not consistent with the behavior of any of the bands observed for In or for Ga, which did not respond to irradiation.

The isotopic shifts of bands were again determined by using the band groupings. The 569.0/579.0 cm^{-1} bands of group 1 show an H/D ratio comparable to the HCC bending mode (ν_5) of free acetylene, 1.332 and 1.354, respectively, and small $^{12}C/^{13}C$ ratios of 1.0046 and 1.0047, respectively, indicating that the HCC bending motion is relatively unperturbed from the free C_2H_2 molecule. The 424.8-cm^{-1} band shows a ^{13}C shift to 417.0 cm^{-1} and a D shift to 405.8 cm^{-1}, characteristic of an Al–C stretching mode.

Discussion

Product group stoichiometries will be identified on the basis of the group behavior with respect to concentration changes and with respect to annealing. The group 1 bands are identified as the 1/1 stoichiometry metal/C_2H_2 (MA) species since they are present under the most dilute reagent conditions and since they do not show any marked concentration dependence with respect to either metal or acetylene. Group 2 bands depend markedly on acetylene concentration, but not on metal concentration leading to the association of group 2 with the MA_2 stoichiometry. Group 3 bands are strongly dependent upon metal concentration but not acetylene concentration, which is expected for species with the stoichiometry M_2A; the group 4 bands for indium are also due to higher metal species. Groups 5–7 with aluminum, are not particularly sensitive to either metal or C_2H_2 concentration and are assigned to other 1/1 stoichiometry species.

Indium. Since the group 13 metals should be chemically similar, it is expected that structures of the M–C_2H_2 complex will be analogous to those predicted for Al–C_2H_2 by Xie, Yates, and Schaefer[3] (Figure 1). Structure **1** vibrations should be characterized by a strong In–C stretch, a less intense C–C stretch, and a stronger CH_2 wag. The observed C–H bending motions of the InA species, at 595.0 and 544.0 cm^{-1}, respectively, are too low to be the CH_2 wag which should appear in the 900-cm^{-1} region based on C_2H_4. Structure **2** is predicted to have intense In—H and C≡C stretching modes. The In—H stretch in HInOH[22] occurs at 1480 cm^{-1}, and there is no intense band observed in this region which can be identified as an In—H motion. The C≡C stretch for $HInC_2H$ is predicted to blue-shift from C_2H_2, which is clearly not the present case. Ab initio calculations also predict large activation barriers for the vinylidene structure **1** and the insertion structure **2** to be obtained.[3,5] It is concluded that neither **1** nor **2** is observed in the In reactions.

The key features of the cis structure **5** and of the trans structure **6** are the M–C stretch along with C–H bending and wagging motions in the 900-cm^{-1} region. Since no appropriate C–H bending and wagging motions were observed in the 900-cm^{-1} region, we must conclude that σ type radical structures **5** and **6** as described by Kasai and McLeod[6,7] were not observed here.

The remaining two candidates are structures **3** and **4**. In terms of vibrational spectroscopy, it is difficult to distinguish between the two; **3** should have two strong In—C stretches, a more intense C—H wag, and a weak C—C stretch at approximately the double-bond C═C stretching position. In contrast, **4** is predicted to have a strong In—C stretch, a strong C—H wag, at least one strong C—H in-plane bend higher still in frequency, and a C—C stretch higher in frequency than predicted for **3**.

The observed major product spectrum is more consistent with **4** than with **3** for several reasons: (1) Only one In–C stretch is observed, at 418.0 cm^{-1}, and it is lower in frequency than any of the observed C–H motions. (2) The more intense C–H motion at 544.0 cm^{-1} is probably an out-of-plane motion. The less intense C–H motion at 595.0 cm^{-1} is most likely the antisymmetric C–H in-plane bending motion. (3) The C–H stretching motion at 3063 cm^{-1} is strongly coupled to the C–C stretching motion, as shown by the large ^{13}C shift. (4) The C–C stretching motion at 1668 cm^{-1} is appropriate for **4** but not **3** on the basis of calculations for the AlC_2H_2 species.[3]

For the other species observed, the dearth of bands precludes positive identification of the structures. A few observations, however, suggest probable structures. Acetylene dimerizes readily in the gas phase to form a "T-shaped dimer", and there is always some amount observable in the matrix.[13] A probable structure for the group 2 InA_2 species is one where the InA subunit is involved in the hydrogen bonding to another solvating acetylene. Manceron and Andrews[9] suggest, in the $Li-(C_2H_2)_2$ case, the proton donor is the solvating acetylene due to the decrease in acidic character of the LiA subunit.

In the case of the group 3 In_2A species, the observed bands are slightly red-shifted from bands assigned to the primary species, indicating analogous structures. The metal dimer is present in the matrix, as evidenced by the $H_2O\cdots In_2$ complex at 1583.0 cm^{-1}.[12] The In_2A structure is likely to be a C_{2v} structure shaped like a butterfly with C_2H_2 as the body and In_2 as the wing tips. The group 4 In_2A' species absorptions are shifted a long way from any of the principle species absorptions, implying a very different structure. In fact, the species may have a different stoichiometry, i.e. In_2A_2 or In_2A_3.

Gallium. The spectroscopy of the group 1 GaA species is very similar to that of the InA species, and it becomes apparent that similar arguments about the structure are applicable. The CCH bending motion is higher in frequency for GaA than for the corresponding InA species, but the H/D ratio is 1.327 versus 1.328 for the InA species. Similarly, the M–C stretch is lower in frequency for GaA than for InA, but the $^{12}C/^{13}C$ ratio is 1.030 versus 1.033, respectively. The C–H stretching frequency shows less ^{13}C shift for GaA than for InA, indicating less C–C interaction with the symmetric stretch in GaA.

The model proposed for the group 2 InA_2 with the metal atom sitting on top of a "T-shaped" acetylene dimer does not account for the observation of two M–C stretches for GaA_2 unless the symmetric and antisymmetric M–C stretching modes are both approximately equal in intensity. The red shifts displayed by the CCH bending, C–C stretching, and C–H stretching modes are consistent with additional involvement of the GaA subunit with another electron-withdrawing entity, specifically the acidic H on another acetylene. If a different model is considered, one where the acetylene subunits are in opposition with the metal in the center, it can be shown that the observed modes should shift in frequency toward the free acetylene values from the GaA values due to a reduced capability of the metal to overlap with each acetylene.

The surprising observation of two M–C stretches for the group 3 Ga_2A species with different $^{12}C/^{13}C$ ratios leads to a quandary. Are the metals both attached to the π bond to give symmetric and antisymmetric stretches perpendicular to the acetylene axis, or is only one metal of a dimer attached to the acetylene to give symmetric and antisymmetric stretching modes? The CCH bending mode shows an H/D ratio similar to the in-plane δ-(CCH) bending mode of the GaA species. The lower frequency indicates that more electron density from the metals is being donated to the acetylene. This supports the perpendicular model similar to the one suggested for In_2A and Li_2A.[9]

It is not possible to envision a model for the Ga_2A' species since the stoichiometry is not certain. The observation of two M–C stretches suggests strongly that the species may involve more than one acetylene, but this could also be a different isomer of Ga_2A.

Aluminum. With only two modes observed for the major product, it is difficult to identify the structure of the AlA species without comparison to theory and the GaA and InA species. Considering the stable, accessible isomers of AlA calculated by Xie, Yates, and Schaefer[3] and the present InC_2H_2 and GaC_2H_2 observations, it is evident that the group 1 AlC_2H_2 product is the π-bonded complex structure **4**. It appears that Al atom exerts a much smaller influence on the bonding of the acetylene subunit than Ga and In. This is supported by the low intensity of the observed bands relative to those observed for the GaA and InA species. It is also supported by the large H/D ratio of the 569.0-cm^{-1} band, which is indicative of a largely unchanged vibrational mode from the corresponding HCC bending mode of free acetylene and the low 424.8-cm^{-1} frequency of the Al–C stretching mode. Comparison with the frequency calculations of Xie, Yates, and Schaefer[3] confirm assignment of the strong 569.0- and 424.8-cm^{-1} group 1 bands to the π complex ($^2B_2$ symmetry; structure **1** in ref 3 and structure **4** here). Calculations (SCF/DZP) predict the strongest infrared bands to be HCC bending and Al–C stretching modes at 643 and 479 cm^{-1}, respectively, and the C–C stretching mode to be a weak band at 1870 cm^{-1}. The calculated frequencies scaled by 0.89 match the observed frequencies, which is appropriate for this level of theory. The weak C–C stretching mode (scaled to 1664 cm^{-1}) could be obscured by water absorptions. In addition, calculations at the CASSCF level predict the strong modes at 603 and 404 cm^{-1} for the π complex,[4] which also support the present assignments.

The remaining aluminum acetylene products were either increased (groups 5 and 8) or produced (groups 6 and 7) by the full light of the medium-pressure mercury arc, and each group behaved differently on successive irradiations. The group 5 band indicated a major codeposition product and first increased and then decreased on photolysis. The 609.0-cm^{-1} band showed the small ^{13}C shift expected for an HCC bending motion, similar to the corresponding group 1 band. The most plausible assignment for the group 5 band is to the $^2A_1$ three-membered ring (structure **3**). The strongest infrared band is the HCC bending mode calculated[3] at 706 cm^{-1}; scaling by 0.86 gives the observed frequency. The weaker Al–C stretching modes calculated at 809 and 713 cm^{-1} probably scale down and are masked by C_2H_2 and CO_2 absorptions.

Theoretical calculations have characterized two different cyclic species, the $^2B_2$ "π complex" and $^2A_1$ three-membered ring; the latter is more stable by 4–6 kcal/mol, and there is only a small barrier (if any) between the two cyclic species.[3-5] Both cyclic species should be formed on codeposition of Al and C_2H_2 with excess argon at 12 K, and the increase of the $^2A_1$ species at the expense of the $^2B_2$ species on photolysis is consistent with their relative stabilities.

The group 6 and 7 bands were photolysis products of the group 1 and 5 bands, but the group 6 bands continued to increase on prolonged photolysis while the group 7 decreased. Both group 6 and 7 bands include a C≡C stretching mode on the basis of the large ^{13}C shifts (70.6 and 71.6 cm^{-1}) and proximity of this mode to that for free acetylene (1973 cm^{-1}). In addition, group 7 includes an Al–H stretching mode at 1804.1 cm^{-1} (no ^{13}C shift and H/D ratio 1.372) and group 6 includes an Al–C stretching mode at 512.8 cm^{-1} (^{13}C shift to 501.9 and D shift to 456.0 cm^{-1}). Ab initio calculations (CISD) give two of the strongest infrared bands of the $HAlC_2H$ insertion product (structure **2**) at 2248 cm^{-1} (C≡C) and 1996 cm^{-1} (Al—H); scaling by 0.89 and 0.90, respectively, predicts the observed 2000- and 1804-cm^{-1} frequencies. The other strong band calculated at 665 cm^{-1} probably falls undetected under the strong group 5 band at 609 cm^{-1}. Group 7 is, therefore, identified as the $HAlC_2H$ insertion product, which requires activation energy for formation.[5] This is consistent with the Al + CH_4 reaction, which also requires photoinitiation.[25] The Al—H stretching mode of $HAlC_2H$ at 1804 cm^{-1} is slightly higher than the 1746-cm^{-1} value for $HAlCH_3$,[25] and the C≡C stretching mode at 2000 cm^{-1} is also slightly higher than the C_2H_2 value (1973 cm^{-1}).

Group 6 is assigned to the photodissociation product H—C≡C—Al on the basis of the observation of C≡C and Al—C stretching and HCC bending modes and the photochemistry. The similar H—C≡C—B species was observed to increase on photolysis at the expense of HBC_2H.[17] Although H—B—C≡C

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is more stable than H—C≡C—B,[17] the aluminum counterparts are expected to be the reverse with H—C≡C—Al more stable because of the weaker Al—H bond compared to B—H.

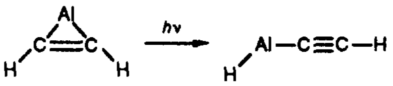
Finally, the group 8 band cannot be identified. It is largely Al–C in character, but it does not fit any of the bands calculated for AlC_2H_2 species.[3] The group 8 band may be due to a dialuminum species.

We have no infrared evidence for the σ-bonded vinyl radicals proposed to explain the ESR spectra of Al + C_2H_2 species in solid neon.[6,7] Calculations predict strong (scaled) bands near 550 cm^{-1} (Al–C stretch) and 900^{-1} (HC bend) for the stable trans radical,[3] and no such bands were observed here. It is possible for a small yield of the trans vinyl radical to be produced sufficient for ESR detection but not IR observation. However, the major Al + C_2H_2 reaction products characterized by infrared spectra are the cyclic $^2B_2$ and $^2A_1$ species, and the major radical photolysis product $HAlC_2H$ has two inequivalent protons. We must note that the reaction to produce the ESR-characterized species required Al atoms to traverse through acetylene vapor before deposition with excess neon;[7] hence some thermal activation is required for this reaction. We suggest that analysis of the ESR spectrum[6,7] be reconsidered in light of the infrared spectrum, the product photochemistry, and theoretical calculations.[3-5]

Conclusions

Ga, In, and Al atoms form adducts with acetylene, which are best characterized as π complexes of C_{2v} symmetry where the metal shares electron density from one C_2H_2 π-bonding orbital. This accounts for the IR activity of the C–C stretching motion, which is red-shifted by about 300 cm^{-1} from that of free acetylene. The metal p-orbital overlap with the acetylene π-bonding orbital seems to increase with increasing size, In > Ga > Al, which is evidenced by the increasing shift in the C–C stretching frequency from Ga (1692 cm^{-1}) to In (1668 cm^{-1}) and by the relatively small change in M–C_2 stretching frequency despite the large mass difference among the metals. Ga and In also form compounds with either two metals and one acetylene or one metal and two acetylenes.

Al gave another major reaction product identified as the three-membered ring on the basis of comparison with ab initio calculations. This is analogous to the borirene radical species observed with boron and acetylene.[17] In addition photolysis in the Al experiments decreased the AlC_2H_2 π complex and produced the insertion product $HAlC_2H$ that was observed to form directly with boron.



Aluminum gives the same major insertion and addition products observed with boron and acetylene in addition to the π complex observed with Ga and In and C_2H_2.

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