

# Low Temperature Matrix Isolation Study of the $\text{Al}(\text{CH}_3)_3 + \text{HN}_3$ Reaction

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## Abstract

The reaction of trimethylaluminum,  $\text{Al}(\text{CH}_3)_3$ , and  $\text{HN}_3$  was experimentally studied in the lab by low temperature matrix isolation. The reactants, each diluted to 1% in argon, were deposited at selected stoichiometric ratios onto a potassium chloride salt window at approximately 10 K. Low temperature matrix isolation eliminated the reaction of the reactants and products with the walls of the reaction vessel. FTIR was used to monitor the presence of chemical species, the reactants and new azide containing species, in the solid argon matrix. Goals of the low temperature matrix isolation study was to observe new species being formed by the appearance of features in the FTIR spectrum that were unique to the reactants and to confirm the identity of the species. Comparison of frequencies to be calculated for likely candidates of products and comparison of the chemical shifts of the products' azide asymmetric stretch from the  $\text{N}_3$  asymmetric stretch of  $\text{HN}_3$  with the frequencies and chemical shifts observed in the FTIR spectrum will be used to identify products.

## Introduction

The formation of aluminum and gallium azides by room temperature reactions followed by their decomposition has been reported as an efficient method for the generation of  $\text{AlN}$  and  $\text{GaN}$  films.

The aluminum system involved reacting  $\text{Al}(\text{CH}_3)_3$  with excess  $\text{HN}_3$ , condensation of

$\text{Al}(\text{N}_3)_3$  as a film, and gently heating the azide film to 400K to produce a film of  $\text{AlN}$ . The stoichiometric reaction of  $\text{Al}(\text{CH}_3)_3$  with excess  $\text{HN}_3$  yielded  $\text{Al}(\text{N}_3)_3$  and methane. The mechanism was a stepwise addition of  $\text{HN}_3$  followed by the elimination of methane that resulted in the fully azidified product,  $\text{Al}(\text{N}_3)_3$ . Steps one and two occurred in the gas phase generating the intermediate species of the reaction,  $\text{Al}(\text{CH}_3)_2(\text{N}_3)$  and  $\text{Al}(\text{CH}_3)(\text{N}_3)_2$ , which were observed by FTIR. The azidified product,  $\text{Al}(\text{N}_3)_3$ , was not observed by FTIR in the gas phase, but was observed by FTIR in low temperature argon matrices. The full azidified product condensed as a film containing  $\text{Al}(\text{N}_3)_3$ , the azide species, as well as the  $\text{Al-N}_2$  complex and  $\text{AlN}$  at 300 K. Gentle heating of the film to 400 K eliminated the  $\text{Al}(\text{N}_3)_3$  and  $\text{N}_2$  from the film resulting in the formation of  $\text{AlN}$  film.<sup>1</sup>

A film of  $\text{GaN}$  was generated by a photochemical induced reaction since the reaction did not proceed stoichiometrically like the  $\text{Al}(\text{CH}_3)_3$  and  $\text{HN}_3$  reaction. The gallium system involved  $\text{HN}_3$  slowly reacting with  $\text{Ga}(\text{CH}_3)_3$  at the surface of the reaction vessel to produce thin film containing azide-substituted gallium compounds at 300 K. Irradiation of the gaseous mixtures of  $\text{HN}_3$  and  $\text{Ga}(\text{CH}_3)_3$  at 253.7 nm dissociated  $\text{HN}_3$  to generate  $\text{NH}(^1\Delta)$  and  $\text{N}_2$  at an increased rate of reaction. The film was heated to 400 K resulting in the elimination of  $\text{N}_2$  and the formation of  $\text{GaN}$  film.<sup>2</sup>

Since there was no evidence of the step-wise addition of  $\text{HN}_3$  observed in the afore mentioned gas phase gallium experiments, a low temperature matrix isolation study was done to probe the reaction of  $\text{Ga}(\text{CH}_3)_3$  and  $\text{HN}_3$ . The reagents, very shortly pre-mixed, were co-deposited at a 1:1 stoichiometric ratio in a low temperature argon matrix. The matrix was annealed to 40 K after the deposition allowing the reagents to move together and react to form a new azide species.

New features, especially those appearing in the azide asymmetric stretch region of 2050-

2150  $\text{cm}^{-1}$ , were monitored by FTIR. New features that appeared in the infrared spectra collected during the annealing process have been tentatively assigned to  $\text{Ga}(\text{CH}_3)_2(\text{N}_3)$ . Ab initio calculations were evaluated to identify the new species formed by the reaction.

Qualitative agreement between the calculated frequencies and the frequency shift of the azide asymmetric stretch from  $\text{HN}_3$  to the new azide compound and the observed frequencies and frequency shift supported the identification of the reaction product as  $\text{Ga}(\text{CH}_3)_2(\text{N}_3)$ , dimethylgallium azide. The results suggested that a stepwise mechanism like that assumed for the  $\text{Al}(\text{CH}_3)_3$  and  $\text{HN}_3$  gas phase reaction, occurred in the non-photolytic reaction between  $\text{Ga}(\text{CH}_3)_3$  and  $\text{HN}_3$ .

To obtain additional support for the assignment of  $\text{Ga}(\text{CH}_3)_2(\text{N}_3)$  as the product of the 1 $\text{Ga}(\text{CH}_3)_3$ :1  $\text{HN}_3$  reaction in an argon matrix, a low temperature matrix isolation study of the  $\text{Al}(\text{CH}_3)_3$  and  $\text{HN}_3$  is being done. The reactants, each diluted to 1% in argon, are deposited on a salt window at approximately 10 K, and the features of the solid argon matrix are monitored by FTIR. Ab initio calculations will be evaluated to confirm the identity of new azide compounds. The observed  $\text{N}_3$  asymmetric stretch will be compared to that obtained from ab initio calculations. The expected product for a 1:1  $\text{Al}(\text{CH}_3)_3$  and  $\text{HN}_3$  reaction is  $\text{Al}(\text{CH}_3)_2(\text{N}_3)$ . If the Ga and Al product assignments are correct, the shifts observed for the  $\text{N}_3$  asymmetric frequency for  $\text{Ga}(\text{CH}_3)_2(\text{N}_3)$  and  $\text{Al}(\text{CH}_3)_2(\text{N}_3)$  should show excellent agreement with the calculated shifts. Other stoichiometric ratios, such as 2:1 and 3:1  $\text{HN}_3$  to  $\text{Al}(\text{CH}_3)_3$ , are also currently being studied to identify all species formed assuming a stepwise mechanism for the  $\text{Al}(\text{CH}_3)_3 + \text{HN}_3$  reaction.

### Experiment

In these experiments, the reaction of  $\text{Al}(\text{CH}_3)_3$  and  $\text{HN}_3$  was studied by low temperature matrix isolation. The reactants were each diluted to 1% in argon and were contained in Pyrex bulbs. The gases were flowed separately at a variety of stoichiometric ratios through Teflon lines. The lines of the system met at a joint where the gases were premixed only for a short period of time and co-deposited on a KCl window in the coldhead. The system lines were at room temperature, and the back-pressure in the lines

was built up to approximately 9 Torr when running an experiment by controlling the amount of vacuum in the lines with an ON/OFF valve. When the pressure in the lines was established, a needle valve was opened, and the reactants were flowed into the coldhead apparatus. (Figure 1).

A solid argon matrix was deposited on the potassium chloride salt window in the coldhead. A CTI-CRYOGENICS 9600 Compressor achieved the low temperature of approximately 10 K inside the coldhead after the pressure of the coldhead was of the order of  $10^{-5}$  Torr. The pressure inside the coldhead was established using a rough pump followed by a differential pump. The product flowed from the system lines to the KCl window of the coldhead due to the extremely low pressure and temperature inside the coldhead, and a matrix was deposited onto the salt window.

The growth of the matrix was monitored by FTIR using a Nicolet Protégé 460 spectrophotometer. The IR beam was passed through the salt windows of the coldhead apparatus (Figure 2). As a matrix deposited on the salt window, an absorbance spectrum was collected every five minutes. Features in the collected IR spectra appeared to "grow in" since the intensity of the absorbance increased as the amount of material deposited on the window increased. The most prominent new features, unique from the reactants, were observed near the azide asymmetric stretch region. The matrix was deposited for approximately one hour.

Figure 1: Experimental apparatus for matrix deposition

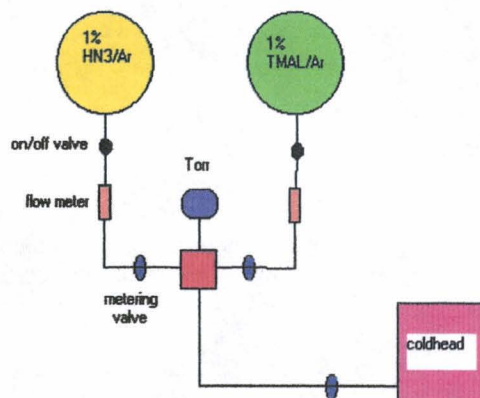
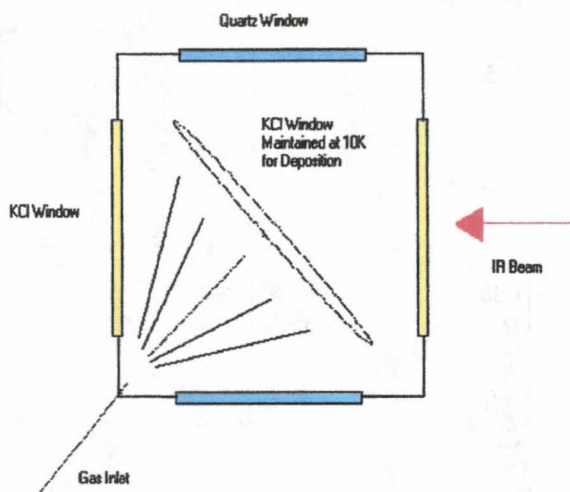


Figure 2: Cross-section of coldhead and IR beam orientation



### Results and Discussion

The reaction of  $\text{Al}(\text{CH}_3)_3 + \text{HN}_3$  was experimentally explored in the lab. Assuming a stepwise addition mechanism like that observed in the aluminum gas phase experiments, it was expected that when different stoichiometric ratios of  $\text{Al}(\text{CH}_3)_3$  and  $\text{HN}_3$  were reacted, azide substituted products would result. Argon matrices containing only  $\text{Al}(\text{CH}_3)_3$  or  $\text{HN}_3$  were deposited, and IR spectra were collected during the deposition. Matrices were deposited at the following stoichiometric ratios: 5  $\text{Al}(\text{CH}_3)_3$ :1  $\text{HN}_3$ , 1  $\text{Al}(\text{CH}_3)_3$ :1  $\text{HN}_3$ , and 1  $\text{Al}(\text{CH}_3)_3$ :2  $\text{HN}_3$  to probe the reaction of  $\text{Al}(\text{CH}_3)_3 + \text{HN}_3$ . Features of the solid argon matrices were monitored by FTIR.

The reactants were deposited in argon matrices onto the coldhead salt window and monitored by FTIR. The collected spectra for each reactant were used as reference data and confirmed the presence of unreacted  $\text{Al}(\text{CH}_3)_3$  and  $\text{HN}_3$  in an argon matrix. Each reactant has unique features observed at particular frequencies in an IR spectrum. The most intense azide feature, the  $\text{N}_3$  asymmetric stretch was observed at  $2137 \text{ cm}^{-1}$ . The features observed in the trimethylaluminum deposition were a mixture of the monomer and dimer species of  $\text{Al}(\text{CH}_3)_3$ . The most prevalent monomer species,

methyl rock, feature was seen at  $737 \text{ cm}^{-1}$ , and the most intense, methyl rock, dimer peak was observed at  $770 \text{ cm}^{-1}$ . The feature, associated with the  $\text{Al}-\text{CH}_3$  asymmetric stretch, observed at  $698 \text{ cm}^{-1}$ , represented a mixture of the monomer and dimer species, and the asymmetric methyl stretches of trimethylaluminum were observed at  $2955$ ,  $2946$ , and  $2903 \text{ cm}^{-1}$  (Figures 3 and 4).

Trimethylaluminum exists primarily as a dimer species at room temperature. When trimethylaluminum was cooled to very low temperatures, the equilibrium of the reaction is reversed to yield the monomer species. The existence of the dimer in the low temperature matrix isolation study resulted from the deposition. When the argon matrix was deposited, a needle valve was opened allowing gas to flow into the coldhead. When the reactant gases were mixed, the needle valve was opened to allow an increased amount of gas to flow into the coldhead. The heat of condensation resulting from the increased amount of gas flowing into the coldhead caused an increase in temperature resulting in a mixture of monomer and dimer species of trimethylaluminum present in the argon matrix.<sup>3</sup>

The reaction of  $\text{Al}(\text{CH}_3)_3 + \text{HN}_3$  was probed by running the 5  $\text{Al}(\text{CH}_3)_3$ :1  $\text{HN}_3$ , 1  $\text{Al}(\text{CH}_3)_3$ :1  $\text{HN}_3$ , and 1  $\text{Al}(\text{CH}_3)_3$ :2  $\text{HN}_3$  experiments. In each experiment an azide product was observed. The products formed by the 5  $\text{Al}(\text{CH}_3)_3$ :1  $\text{HN}_3$  and the 1  $\text{Al}(\text{CH}_3)_3$ :1  $\text{HN}_3$  experiments are assumed to be the same, mono-substituted azide product,  $\text{Al}(\text{CH}_3)_2(\text{N}_3)$  (Figures 5 and 6). The collected IR spectra for each experiment exhibited strong features in the azide asymmetric stretch region at  $2176$ ,  $2169$ ,  $2157$ ,  $2148$ , and  $2138 \text{ cm}^{-1}$ , shifted to the blue of the  $\text{HN}_3$  azide asymmetric stretch. The product of the 1  $\text{Al}(\text{CH}_3)_3$ :2  $\text{HN}_3$  reaction had unique features in the azide asymmetric stretch region at  $2160$  and  $2135 \text{ cm}^{-1}$  (Figure 7). This experiment was also thought to have unique features from the prior experiments at  $2832$  and  $2821 \text{ cm}^{-1}$ . A comparison of the IR data of the three experiments may be seen in Figure 8.

Figure 3:  $\text{Al}(\text{CH}_3)_3$   
a). 3000-2850  $\text{cm}^{-1}$

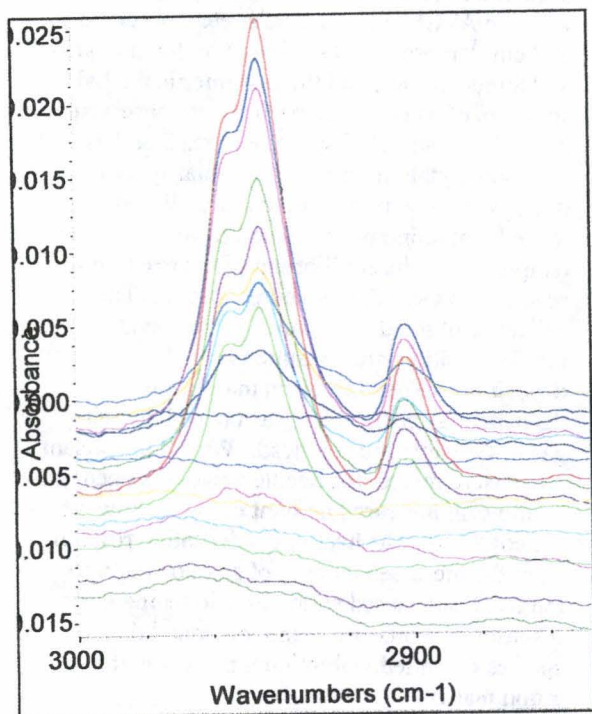


Figure 4:  $\text{HN}_3$   
a). 2200-2000  $\text{cm}^{-1}$

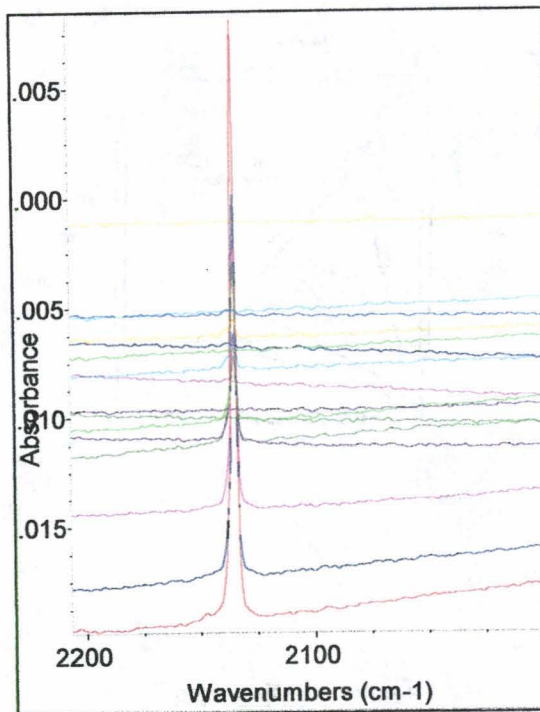


Figure 3:  
b). 800-650  $\text{cm}^{-1}$

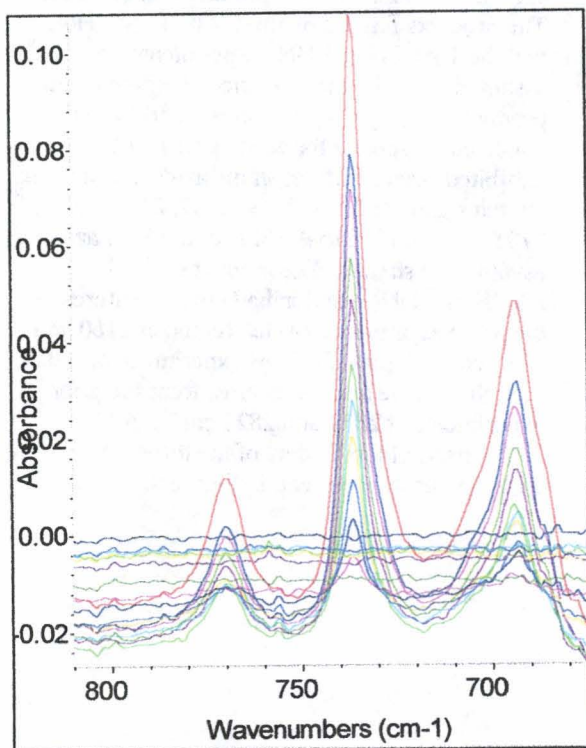


Figure 5: 5  $\text{Al}(\text{CH}_3)_3$ :1  $\text{HN}_3$   
a). 3000-2850  $\text{cm}^{-1}$

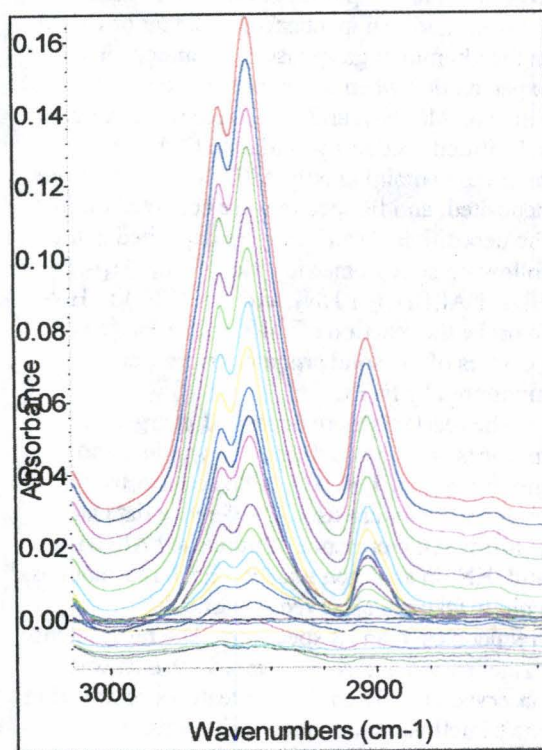


Figure 5:  
b). 2200-2000  $\text{cm}^{-1}$

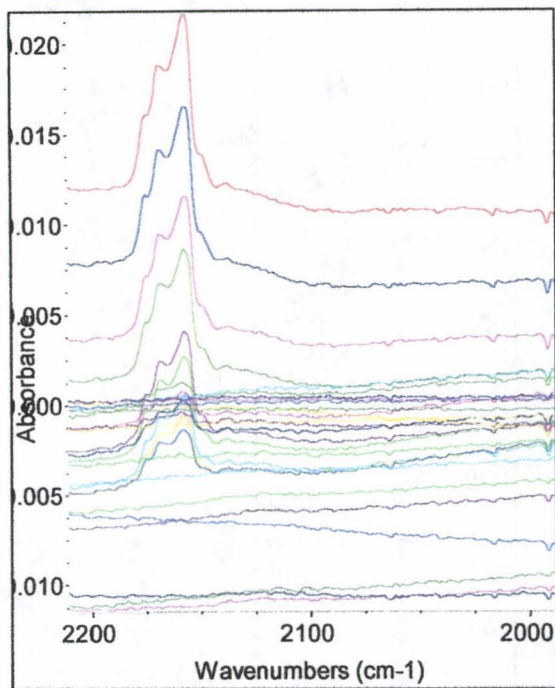


Figure 6: 1  $\text{Al}(\text{CH}_3)_3$ :1  $\text{HN}_3$   
a). 3000-2850  $\text{cm}^{-1}$

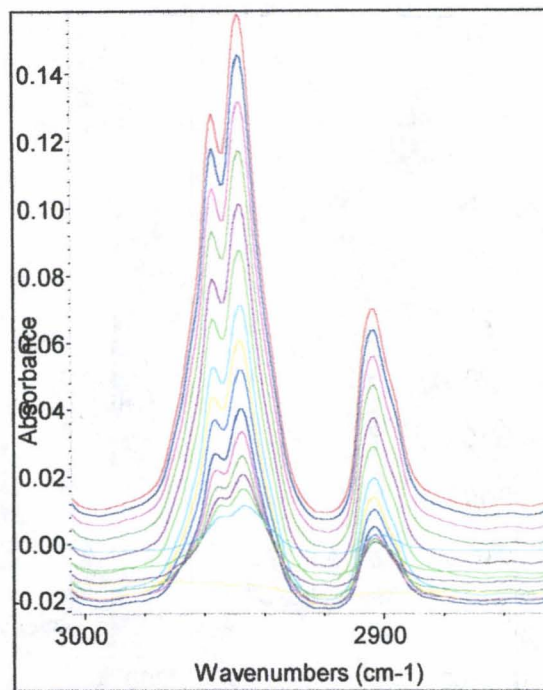


Figure 5:  
c). 800-650  $\text{cm}^{-1}$

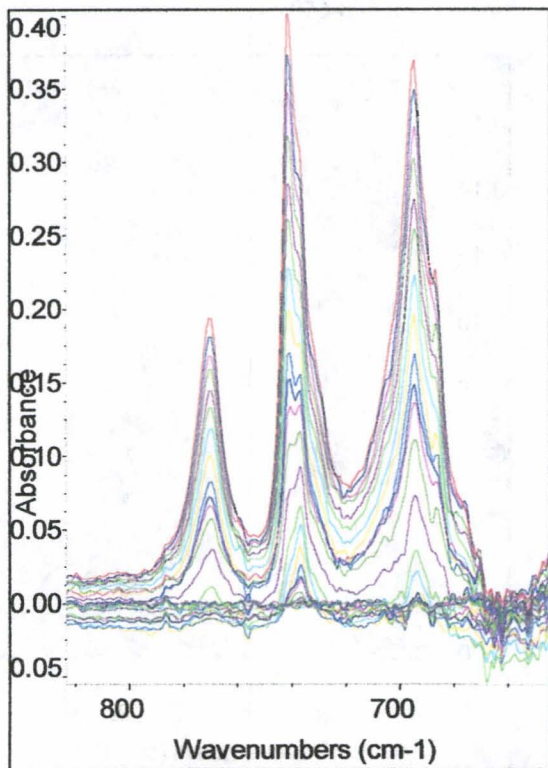


Figure 6:  
b). 2200-2000  $\text{cm}^{-1}$

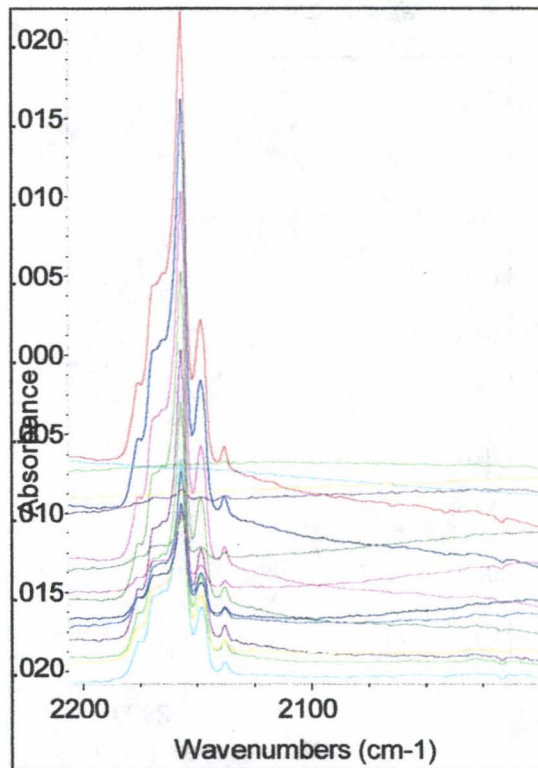


Figure 6:  
c). 800-650  $\text{cm}^{-1}$

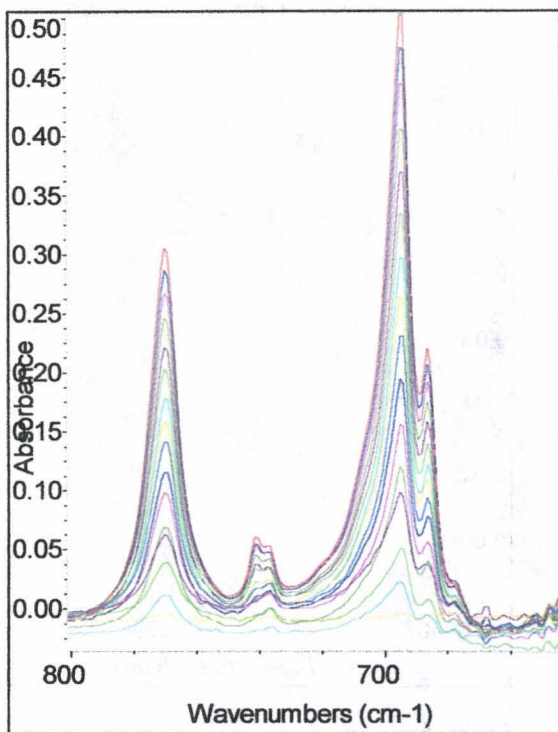


Figure 7:  
b). 2200-2000  $\text{cm}^{-1}$

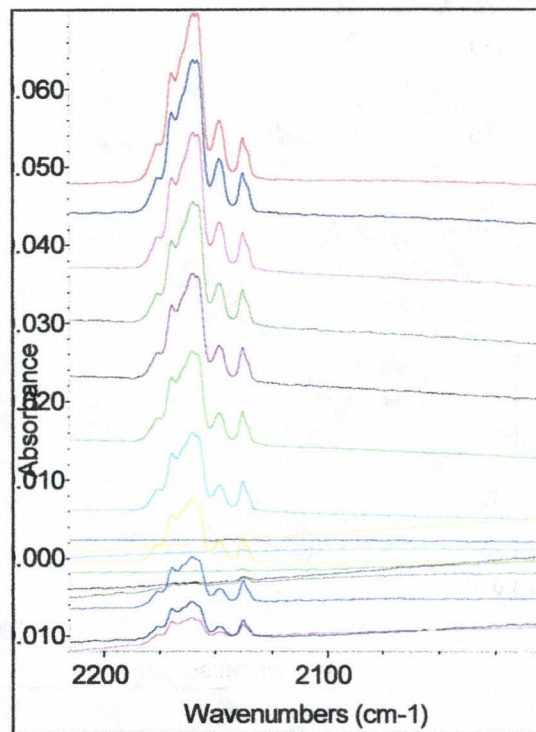


Figure 7: 1  $\text{Al}(\text{CH}_3)_3:2 \text{HN}_3$   
a). 3000-2850  $\text{cm}^{-1}$

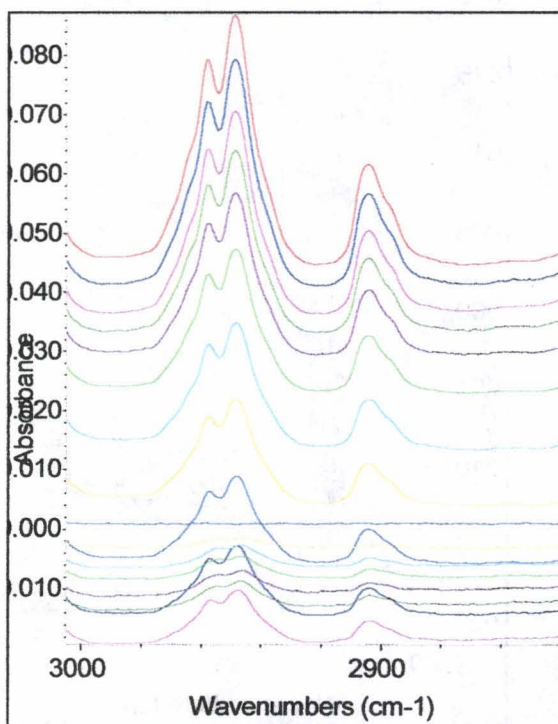


Figure 7:  
c). 800-650  $\text{cm}^{-1}$

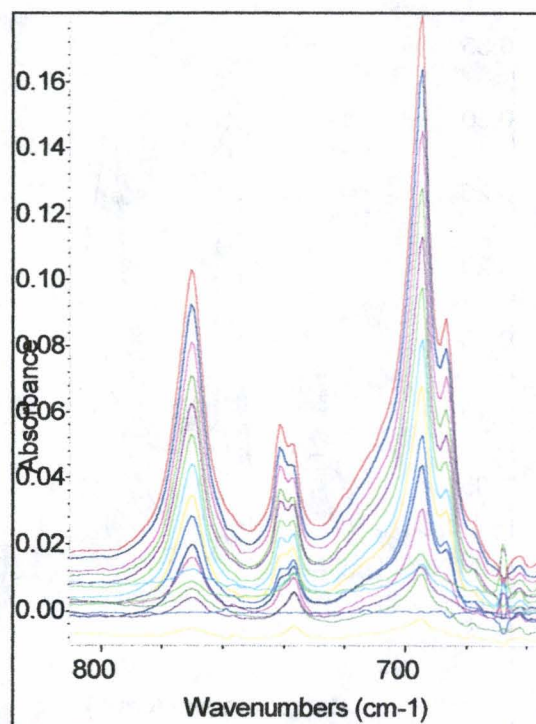


Figure 8: Comparison of the methyl and azide regions of all stoichiometric ratios  
 a). 3000-2850  $\text{cm}^{-1}$

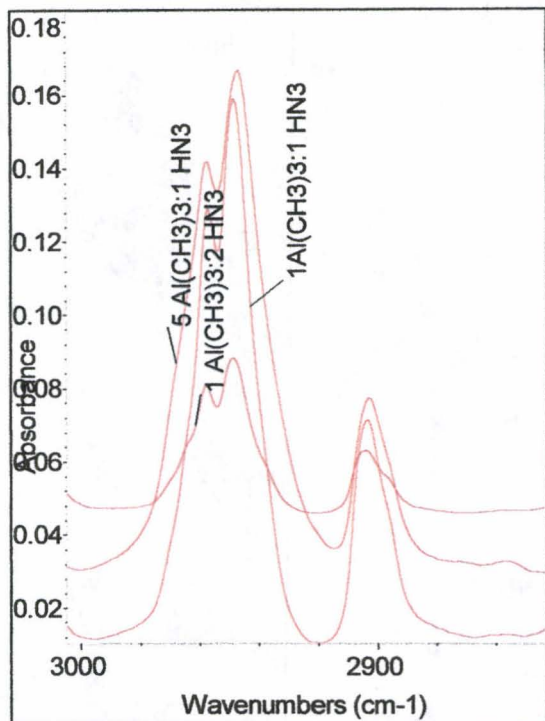
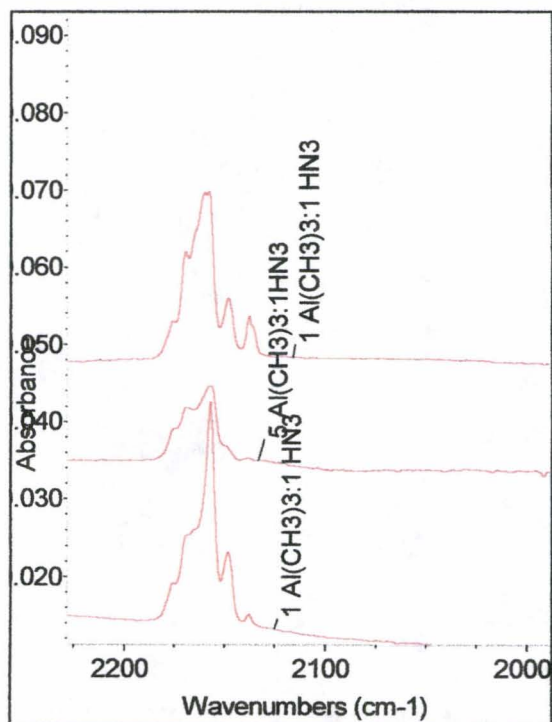


Figure 8:  
 b). 2200-2000  $\text{cm}^{-1}$



## Conclusion

New species were formed in both the trimethylaluminum and trimethylgallium gas phase experiments. Each species exhibited unique features in FTIR spectra and each new species was thought to contain an azide due to the strong feature that appeared in the azide region of the spectrum, 2050-2150  $\text{cm}^{-1}$ . Also note that these features disappeared when the reaction stoichiometry was greater than 2.5:1,  $\text{HN}_3:\text{Al}(\text{CH}_3)_3$  or  $\text{Ga}(\text{CH}_3)_3$  due to the formation of the fully azidified product. Low temperature matrix isolation and ab initio calculations were used to tentatively assign the intermediate species of the trimethylgallium and  $\text{HN}_3$  reaction as  $\text{Ga}(\text{CH}_3)_2(\text{N}_3)$  due to the agreement between observed and calculated frequencies and frequency shifts. Low temperature matrix isolation was used to study the trimethylaluminum and  $\text{HN}_3$  reaction. Different stoichiometric ratios have been experimentally studied. New azide species were observed.

## Acknowledgements

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## References

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