# REPORT DOCUMENTATION PAGE

*Form Approved*
*OMB No. 0704-0188*

| | | |
|---|---|---|
| **1. REPORT DATE** *(DD-MM-YYYY)* | **2. REPORT TYPE**<br>Annual AFOSR Report | **3. DATES COVERED** *(From - To)*<br>10/1/2013 – 09/30/2014 |

**4. TITLE AND SUBTITLE**

Ionic Liquid Fuels for Chemical Propulsion

**5a. CONTRACT NUMBER**

**5b. GRANT NUMBER**

**5c. PROGRAM ELEMENT NUMBER**

**6. AUTHOR(S)**

Stefan Schneider

**5d. PROJECT NUMBER**

**5e. TASK NUMBER**

**5f. WORK UNIT NUMBER**
Q0RA

**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**

Air Force Research Laboratory (AFMC)
AFRL/RQRP
10 E. Saturn Blvd.
Edwards AFB, CA 93524

**8. PERFORMING ORGANIZATION REPORT NO.**

**AFRL-RQ-ED-TP-2014-301**

**9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)**

Air Force Research Laboratory (AFMC)
AFRL/RQR
5 Pollux Drive
Edwards AFB, CA 93524

**10. SPONSOR/MONITOR'S ACRONYM(S)**

**11. SPONSOR/MONITOR'S REPORT NUMBER(S)**
**AFRL-RQ-ED-TP-2014-301**

**12. DISTRIBUTION / AVAILABILITY STATEMENT**
Approved for public release; distribution unlimited

**13. SUPPLEMENTARY NOTES**
AFTC 412 TW PA Clearance #: 14562

**14. ABSTRACT**

Task I: Our proposed research for this task focuses on three distinct first year objectives with second- and third-year priorities dependent upon results from the first year:

1. Investigate the reaction of ABH with varying amounts of $[NCBH_3]^-$ and determine the composition of the mixtures.
2. Prepare pure heterocyclic-$BH_4$ salts and investigate their reactions with ABH.
3. Design and synthesize amine-functionalized IL cations suitable to form stable coordination compounds with metal borohydrides.

Task II: In order to understand the unusual phenomenon of hypergolicity in energy dense materials, a detailed understanding of the reactive intermediate chemistry is required. Towards these ends, the following objectives are pursued:

1. Identify pre-ignition mechanisms and heterogeneous reactivity of next generation ionic liquid (IL) hypergols by infrared spectroscopy.
2. Determination of ionic liquid vaporization and reaction mechanisms by tunable VUV spectroscopy.
3. Determination of ionic liquid hypergolic ignition delay model parameters and reaction pathways via chemical kinetics measurements and molecular dynamics simulations.

**15. SUBJECT TERMS**

| **16. SECURITY CLASSIFICATION OF:** | | | **17. LIMITATION OF ABSTRACT** | **18. NUMBER OF PAGES** | **19a. NAME OF RESPONSIBLE PERSON**<br>Stefan Schneider |
|---|---|---|---|---|---|
| **a. REPORT**<br>**Unclassified** | **b. ABSTRACT**<br>**Unclassified** | **c. THIS PAGE**<br>**Unclassified** | SAR | 27 | **19b. TELEPHONE NO**<br>*(include area code)* |

**Standard Form 298 (Rev. 8-98)**
**Prescribed by ANSI Std. 239.18**

**LRIR #: 14RQ11COR**

**Title:** **IONIC LIQUID FUELS FOR CHEMICAL PROPULSION**

| | |
|---|---|
| **Reporting Period:** | **01 October 2013 – 30 September 2014** |
| **Laboratory Program Manager and Laboratory Principal Investigator:** | **Dr. S. Schneider** |
| **Commercial Phone:** | **(661) 275 5759, DSN: 525 5759** |
| **FAX:** | **(661) 275 5471** |
| **Mailing Address:** | **10 E. Saturn Blvd, Bldg 8451**<br>**Edwards AFB, CA 93524-7680** |
| **E-Mail Address:** | **stefan.schneider@us.af.mil** |
| | |
| **AFOSR Program Manager:** | **Dr. Michael Berman** |

## TABLE OF CONTENTS

# 1.0 RESEARCH GOALS AND OBJECTIVES FY14

## 1.1 TASK I:

Our proposed research for this task focuses on three distinct first year objectives with second- and third-year priorities dependent upon results from the first year:

1. Investigate the reaction of ABH with varying amounts of $[NCBH_3]^-$ and determine the composition of the mixtures.
2. Prepare pure heterocyclic-$BH_4$ salts and investigate their reactions with ABH.
3. Design and synthesize amine-functionalized IL cations suitable to form stable coordination compounds with metal borohydrides.

## 1.2 TASK II:

In order to understand the unusual phenomenon of hypergolicity in energy dense materials, a detailed understanding of the reactive intermediate chemistry is required. Towards these ends, the following objectives are pursued:

1. Identify pre-ignition mechanisms and heterogeneous reactivity of next generation ionic liquid (IL) hypergols by infrared spectroscopy.
2. Determination of ionic liquid vaporization and reaction mechanisms by tunable VUV spectroscopy.
3. Determination of ionic liquid hypergolic ignition delay model parameters and reaction pathways via chemical kinetics measurements and molecular dynamics simulations.

# 2.0 TECHNICAL SUMMARY

## 2.1 INTRODUCTION

### 2.1.1 TASK I

The ionic liquid (IL) program at the Air Force Research Laboratory is investigating tailored energy-dense liquids to provide a scientific foundation for the advancement of the performance and operability envelopes of current propulsion systems. General efforts involve the discovery of energetic ILs based on heterocyclic and open-chain cations in combination with reactive anions. A major goal has been the development of IL fuels which undergo hypergolic ignition upon contact with common propulsion oxidizers. In state-of-the-art bipropellant systems, $N_2H_4$ is the fuel and $N_2O_4$ is the oxidizer. Both compounds are highly toxic, hydrazine being a suspected carcinogen. Replacing hydrazine with an ionic liquid which generally possesses very low volatility, and therefore virtually no vapor toxicity, would be extremely desirable if not already critical. At the same time, the toxic oxidizer should be exchanged for a high-performing, environmentally benign oxidizer like, perhaps, hydrogen peroxide (decomposition of hydrogen peroxide affords only oxygen and water), if other desired properties, especially hypergolic reactivity with the fuel, can be retained. So far, most researchers seeking hypergolic fuels have limited themselves to the extremely toxic and corrosive nitric acid solutions. While important questions remain unanswered, we are exploring new ground. During our previous work we demonstrated the hypergolicity of ILs with one class of hydrogen-rich anions toward a variety of common propellant oxidizers, including hydrogen peroxide. However, for practical purposes the materials had several shortcomings, especially poor liquid range and viscosity. Furthermore, their high hydrocarbon content limits propellant performance. Based on multiple molecular design strategies the proposed research effort focuses on synthesizing novel energetic ILs, supported by experimental mechanistic studies and computational investigations. Expanding on our previous work we intend to enlarge the chemical landscape of known light metal hydride ILs. We envision the successful completion of this project will result in:

- Fundamental understanding of the coordination of light metals in highly reducing environments.
- Expansion of the range of materials available for hydrogen storage.
- Novel solvent systems enabling unique reduction reactions.

### 2.1.2 TASK II

The Ionic Liquids Ignition program investigates the chemical kinetics and reaction dynamics involved in the hypergolic and catalytic ignition of ionic liquid propellants with the purpose of identifying key intermediates and kinetic bottlenecks which can enhance or restrict performance in ionic liquid-based propulsion systems. In better understanding the energy landscape involved in hypergolic ignition of ionic liquids with various oxidizers, we can use this knowledge to support the synthetic efforts in Task I to discover viable candidate ionic liquid fuels for propulsion systems. An important goal of our research is to use sensitive and selective experimental probes to understand in real time and at the molecular level the underlying chemistry involved under relevant extreme environments. The experimental data will provide the necessary mechanistic and chemical kinetics information, and with ab initio quantum chemical analysis, accurate reaction mechanisms will be elucidated. The combined information will feed into chemical kinetics models, which will make reactivity predictions possible for hypergolic fuels and high-temperature catalysts, leading to improved design of energetic ILs including more reliable ignition and sustained combustion.

## 2.2 RESEARCH RESULTS

### 2.2.1 TASK I.

Aluminum borohydrides provide an attractive framework for high hydrogen content ILs. Previously we reported an IL containing the $[Al(BH_4)_4]^-$ anion but the material has several shortcomings which make it impractical to use as a propellant. In an attempt to lower the viscosity, neutral ABH was mixed with an IL containing the cyanoborohydride anion. ILs with the $[NCBH_3]^-$ anion by itself generally possess very low viscosities (~20cp). It was anticipated that the combination of $[NCBH_3]^-$ with ABH would produce a new anion of the formula $[Al(BH_4)_3NCBH_3]^-$. A couple of possibilities were considered for the binding/coordination of the $[NCBH_3]^-$ anion to ABH. Boron and aluminum can compete for the carbon and nitrogen and calculations revealed that boron prefers carbon by ~13kcal/mol. Direct coordination of the CN group to aluminum is also preferred over 3-centered-2-electron hydrogen bonds by ~21kcal/mol (Figure 1).

However, during our previous studies we discovered that the reaction chemistry of ABH is far more complex than initially anticipated and our initial findings prompted us to investigate this chemistry in more detail.

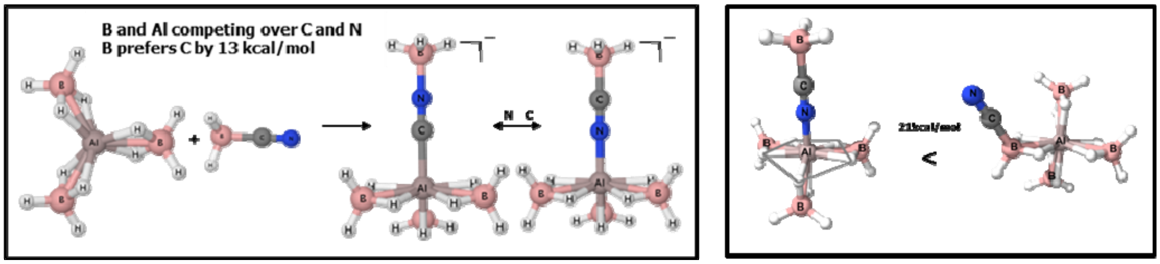


**Figure 1.** *Different coordination possibilities of $[NCBH_3]^-$ to ABH.*

In a principal experimental finding, we established the existence of a prevalent mixed borohydride/cyanoborohydride aluminum compound with a coordination number of seven (Figure 2) and saw spectroscopic evidence that other species are present.

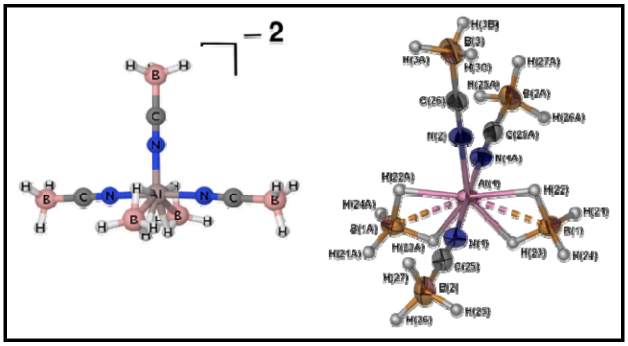


**Figure 2.** *A new, doubly charged anion (calc., left; crystal structure, right) $[Al(BH_4)_2(NCBH_3)_3]^{2-}$*

A number of reactions leading to the formation of the dianion and involving other mixed ligand aluminum coordination compounds, neutral as well as ionic, may be hypothesized. Some preliminary gas phase calculations of the heats of reaction (kcal/mol) help to distinguish these possibilities (Eq. 1-6). As can be seen from the values of equations 1, 3, and 5, no reaction sequence for the formation of the dianion is overwhelmingly preferred.

$$4\ Al(BH_4)_3 + 4\ [NCBH_3]^- \xrightarrow{-103} 2\ [Al(BH_4)_4]^- + [Al(NCBH_3)_3(BH_4)_2]^{2-} + Al(NCBH_3)(BH_4)_2 \quad (1)$$

$$[NCBH_3]^- + Al(BH_4)_3 \xrightarrow{+17} Al(NCBH_3)(BH_4)_2 + [BH_4]^- \quad (2)$$

$$2Al(BH_4)_3 + 2[NCBH_3]^- \xrightarrow{-98} 2[Al(NCBH_3)(BH_4)_3]^- \quad (3)$$

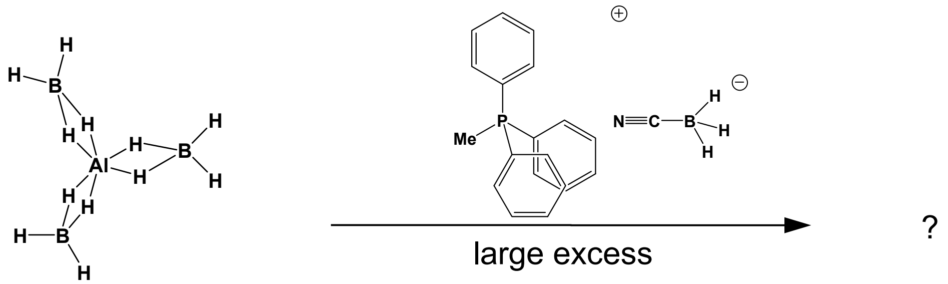
$$[Al(NCBH_3)(BH_4)_3]^- + [NCBH_3]^- \xrightarrow{+3} [BH_4]^- + [Al(NCBH_3)_2(BH_4)_2]^- \quad (4)$$

$$2\ Al(BH_4)_3 + 2\ [NCBH_3]^- \xrightarrow{-96} [Al(BH_4)_4]^- + [Al(NCBH_3)_2(BH_4)_2]^- \quad (5)$$

$$[Al(NCBH_3)_2(BH_4)_2]^- + [CNBH_3]^- \xrightarrow{+18} [Al(NCBH_3)_3(BH_4)_2]^{2-} \quad (6)$$

Furthermore, the isolation of the mixed ligand $[Al(NCBH_3)_3(BH_4)_2]^{2-}$ dianion suggested that a whole new class of hydrogen-rich anions with coordination numbers of six, seven, or eight can be prepared.

In a next step we first explored the synthetic accessibility of new anions of aluminum by reacting ABH with a large amount of $[NCBH_3]^-$.



***Scheme 1**. Reaction of ABH with Methyl-triphenyl-phosphonium CBH.*

The peak integration of the $^1H$ NMR of the isolated product indicated that the species formed should have a cation to anion proton ratio of 15:3:6, 30:6:12, 45:9:18 etc (Figure 3). None of these ratios would fit any of the anionic species shown in equation 1 through 6.

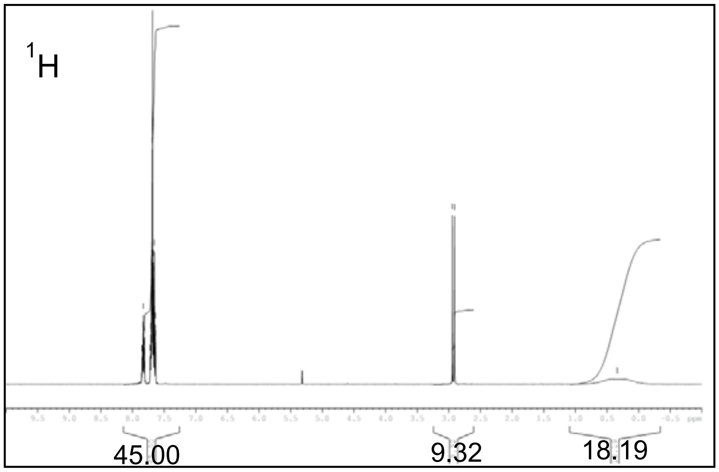


***Figure 3.** $^1H$ NMR of the isolated product after treatment of ABH with a 9 fold excess CBH.*

Coupled $^{11}B$ NMR spectra were recorded at different stages during the addition (Figure 4). For an easier comparison the spectra of the cyanoborohydride (CBH) and aluminumborohydride (ABH) starting materials are depicted as well. It appears that after the addition of 9 equivalents of CBH there is only 1 distinctive species present in solution.

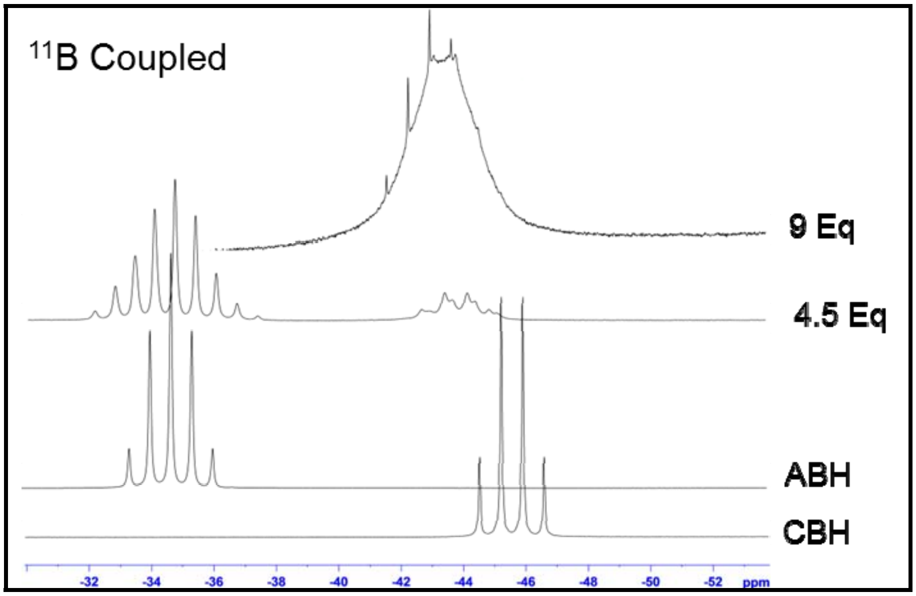


***Figure 4.*** *$^{11}B$ NMR of different stages of the CBH addition process. Spectra of CBH and ABH starting materials are shown for comparison.*

This observation becomes even more obvious when comparing the $^{11}B$ NMR proton decoupled spectra (Figure 5). After the addition of only 4.5 equivalents of CBH (Figure 5 bottom), multiple boron species are still present in solution. After 9 equivalents have been added, only one broad signal is visible in the spectrum.

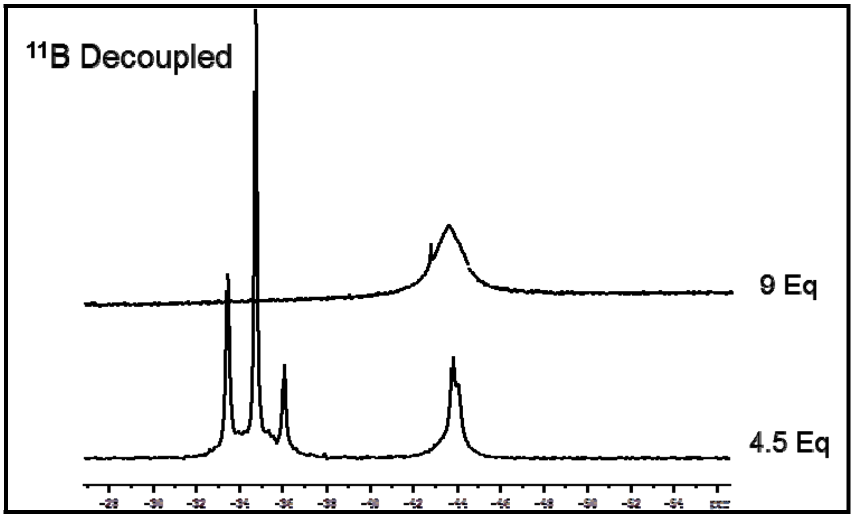


***Figure 5.*** *$^{11}B$ NMR proton decoupled showing the presents of multiple boron species which are converging into one single species after the addition of 9 equivalent CBH.*

Figure 6 shows the $^{27}$Al NMR spectra of the ABH diethyletherate starting material, the reaction mixture after the addition of 4.5 equivalents of CBH as well as the isolated product. While signals with protons in close vicinity to an aluminum core are usually broad (ABH etherate, bottom spectrum) the signal of the isolated product is very sharp.

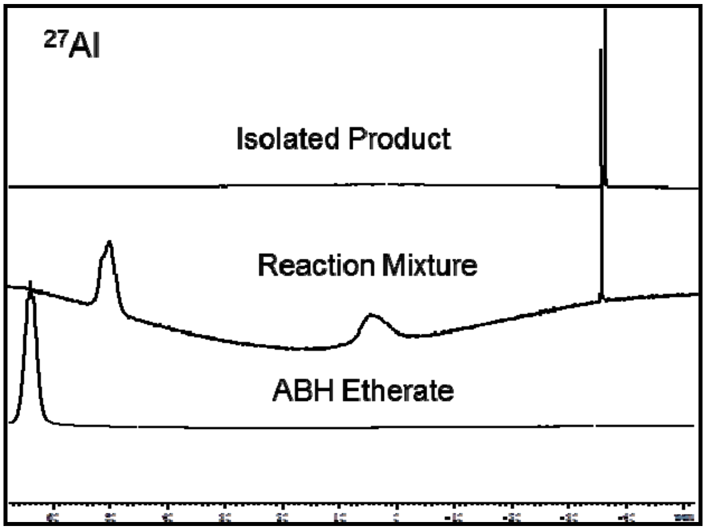


***Figure 6.*** *$^{11}$B NMR of different stages of the CBH addition process. Spectra of CBH and ABH starting materials are shown for comparison.*

Final composition of the isolated product was resolved by a single crystal X-ray structure determination and the structure of the novel $[Al(CNBH_3)_6]^{3-}$ anion is shown in Figure 7.

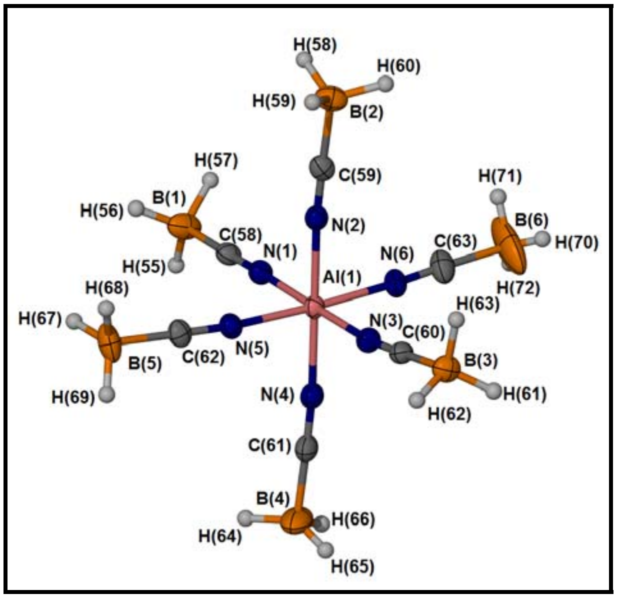


***Figure 7.*** *X-ray crystal structure of isolated product showing a rare example of a hexacoordinated, triply charged aluminum anion.*

Encouraged by these findings, we will investigate anions with the potential of multiple coordination sites, using for example the cyanide or dicyanamide anion. With multiple sites to attach ABH groups, these will increase the overall hydrogen content of the anion. Preliminary calculations indicated that an anion consisting of two ABH molecules bridged by a cyanide anion is vibrationally stable (Figure 8).

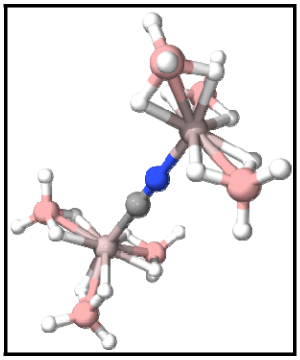
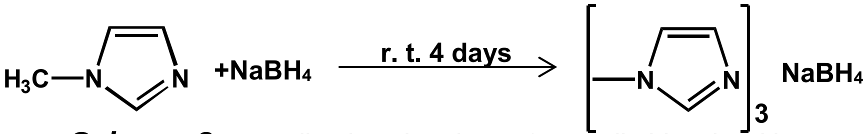


***Figure 8.*** *Calculated configuration of the* $[Al(BH_4)_3CNAl(BH_4)_3]^-$ *anion.*

As mentioned in the introduction, pairing alkylammonium cations with the $[Al(BH_4)_4]^-$ anion produces materials which are only nominally liquids. In many cases, heterocyclic cations such as substituted imidazolium are better liquefying cations than substituted ammonium cations and their two nitrogen substitution sites allow for a reduced hydrocarbon content with an increase in performance. While it was our full intent to prepare $[Al(BH_4)_4]^-$ ILs with substituted imidazolium cations in the previous effort, we were challenged by the synthesis of the necessary precursor materials, imidazolium-$BH_4^-$ salts. Although there were two preparations in the literature,[1] we were unable to reproduce the published results.

In 2012 the group of Ingo Krossing investigated these procedures in great detail and determined that the best material obtainable thereby still had a halide content of at least 22.5%.[2] In addition they discovered a new method for preparing analytically pure borohydride salts in a mixed solvent system, liquid ammonia/methylene chloride, at low temperatures. We now discovered another method which allows us to run the metathesis in a single solvent at room temperature.

We took advantage of the unique coordination possibilities of alkali metal borohydrides. While many coordination complexes of amines with various alkali metal borohydrides are known, the chemistry between methylimidazole and sodium borohydride had not been investigated yet. Methylimidazole coordinates in a 3:1 ratio with sodium borohydride (Scheme 2).



***Scheme 2****. Coordination chemistry of methylimidazole with* $NaBH_4$*.*

Numerous coordination ratios have been observed for amine alkali-metal borohydride complexes. Mono-, bi-, and tridentate for the borohydride to the metal centrum and 1:1, 1:2, 1:3, 2:3 or other odd numbers of metal centrum to amine ligand, depending on the type of amine utilized. Single crystal X-ray structure determinations can provide a definite answer to what type of coordination complex is present. Figure 9 shows the single crystal structure of the coordination complex between methylimidazole and sodium borohydride, revealing a tridentate coordination of the borohydride hydrogens to sodium and an overall coordination number of 6 for the central sodium atom, meaning three amine ligands are coordinated to sodium as well.

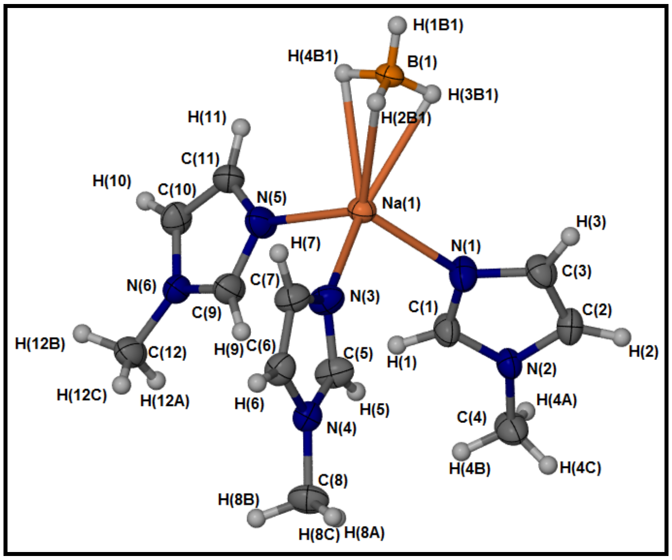
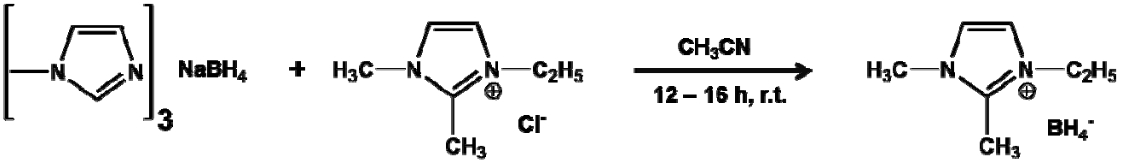


***Figure 9.*** *Single crystal X-ray structure of the coordination complex methylimidazole:$NaBH_4$.*

This coordination complex possesses a distinct characteristic which is not found in uncoordinated $NaBH_4$. While $NaBH_4$ is soluble only up to ~ 2% in acetonitrile the coordination complex with methylimidazole revealed a high solubility in this solvent. Many heterocyclic halide salts are soluble in acetonitrile as well. Therefore, the new coordination complex could be used in metathesis reaction with the formation of sodium chloride and the free amine (Scheme 3). The free amine could be easily removed by washing the product with diethylether.



**Scheme 3.** *Metathesis reaction between heterocyclic halide salt and $NaBH_4$ coordination complex.*

Our new method has multiple advantages over the procedure developed by Krossing. Krossing has to rely on a co-solvent system, between ammonia and methylene chloride. Reactions have to be carried out at low temperature. Methylene chloride has more handling restrictions and health issues than acetonitrile.

Utilizing our method we were also able to obtain the very first single crystal X-ray structure of an asymmetric imidazolium-$BH_4^-$ salt (Figure 10).

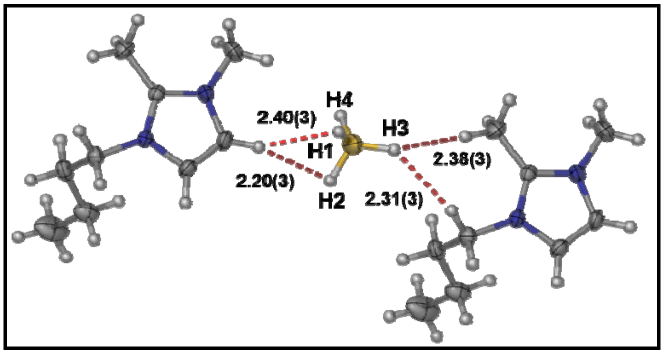


***Figure 10.*** *X-ray structure of 1,2-dimethyl-3-butyl-imidazolium $BH_4^-$ showing H•••H contacts.*

This new synthetic route to analytically pure heterocyclic borohydride salts provides the necessary starting materials for an easy conversion to a new class of ILs with complexed $[Al(BH_4)_4]^-$ anion. Finally the physical properties of this interesting anion when combined with a "classical" IL cation can be established.

## Computational

Energy profiles of reactions either observed or predicted will be determined using quantum chemical methods. Preliminary simulations have uncovered some of the rich chemistry inherent in the aluminum borohydrides. Oxidation by water of either the simple borohydride anion or the neutral borane molecule in the gas phase produces hydrogen gas with the formation of a boron-oxygen bond and takes place via the transition states displayed in Figure 11.

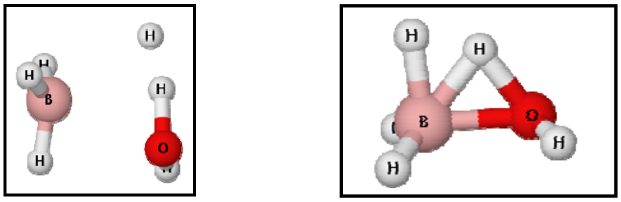


**Figure 11.** Transition states of $BH_4^-$-$H_2O$ and $BH_3$-$H_2O$.

It appears that oxidation of the aluminum borohyride anion, $[Al(BH_4)_4]^-$, does not occur directly in an analogous manner. Rather, a two-step reaction in which water initially displaces a neutral borane molecule (Figure 12, left) and subsequently reacts with it in a complex with the remaining anion (Figure 12, right) is observed in the calculation.

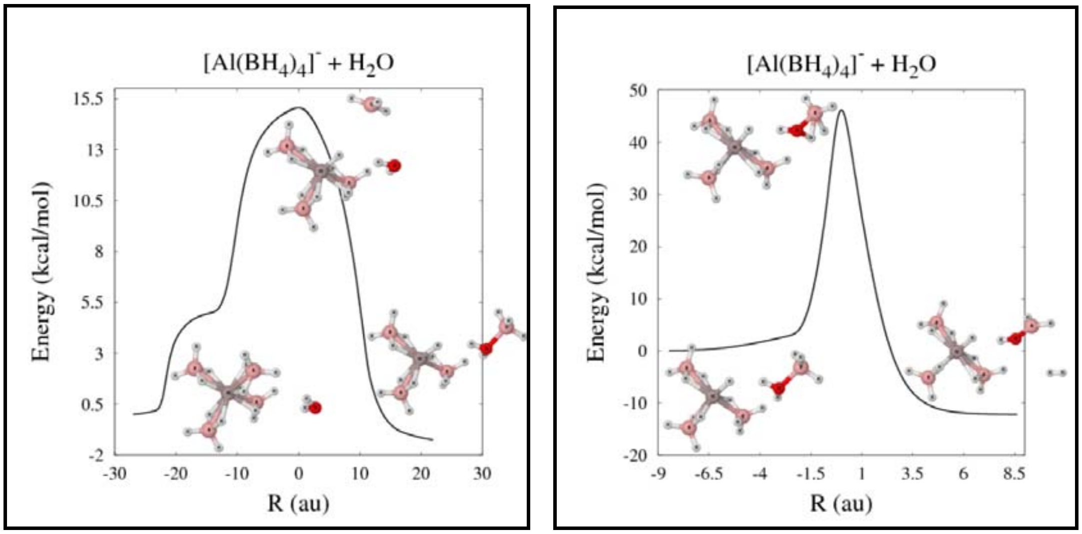


**Figure 12.** Energy profiles along the Intrinsic Reaction Coordinate (IRC) for the hydrolysis of the $[Al(BH_4)_4]^-$.

Additional insight into the relative reactivities of these species is gained from the calculated activation barriers and reaction energies given in Table 1. Although hydrolysis of $[Al(BH_4)_4]^-$ nominally involves oxidation of $BH_3$, the presence of the intermediate anionic fragment leads to an activation barrier and reaction energy in between those for bare neutral $BH_3$ and the bare $[BH_4]^-$ anion. These values agree with the facts that neutral boranes are pyrophoric in moist air, that many aqueous borohydride solutions have substantial stability, and that aluminum borohydride ILs manifest considerable hydrolytic stability, perhaps intermediate between the two. Theory will help the experimental effort by predicting early intermediates such as $[H\text{-}Al\text{-}(BH_4)_3]^-$, and modeling their vibrational spectra as an aid to identifying the species evolving in cryogenic matrices.

**Table 1.** Energies (kcal/mol) for the reactions which form $H_2$ by hydrolysis.

| | Activation energy $E_a$ | Reaction energy $\Delta E$ |
|---|---|---|
| $BH_3$ | 39 | -21 |
| $[H\text{-}Al\text{-}(BH_4)_3]^- + BH_3$ | 46 | -12 |
| $[BH_4]^-$ | 69 | +4 |

## 2.2.2 REFERENCES TASK I

1 a) Wang, J.; Song, G.; Peng, Y.; Zhu, Y. *Tetrahedron Lett.* **2008**, *49*, 6518-6520; b) Zhang, Y.; Shreeve, J.M. *Angew. Chem. Int. Ed.* **2011**, *50*, 935-937.
2 Bürchner, M.; Erle, A.M.T.; Scherer, H.; Krossing, I. *Chem. Eur. J.* **2012**, *18*, 2254-2262.

### 2.2.3 TASK II.

**Al and B nanoparticle infused ionic liquids**

Professor Scott Anderson has developed a method to ball mill aluminum and boron in hypergolic ionic liquids to produce metal nanoparticles coated with the IL that effectively passivates the surface of the metals from oxidation.[1] Professor Anderson has provided several samples to investigate by rapid scan FTIR spectroscopy: Drop tests with $HNO_3$ on these mixtures as a function of nanoparticle loading were performed (Figure 1a), and the ignition delay times are seen in Figure 1b.

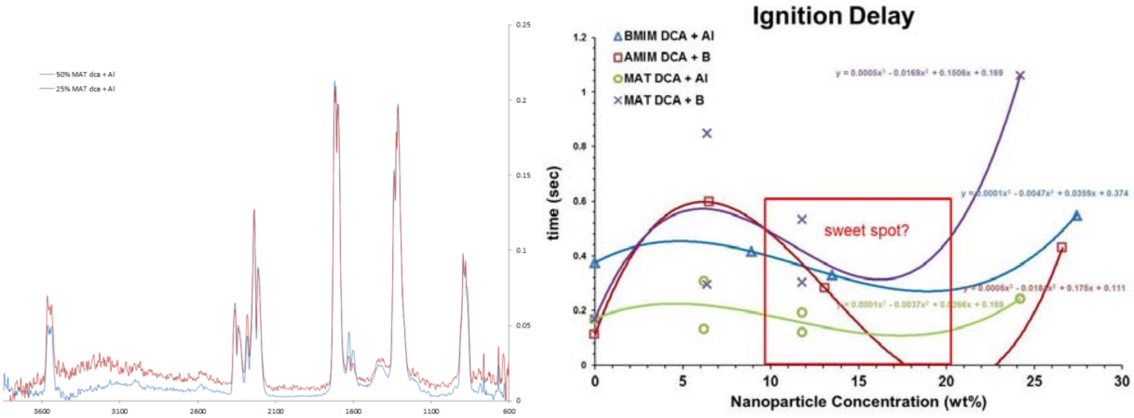


***Figure 1.*** *a) Rapid scan FTIR spectroscopy of 25% $MAT^+dca^-$ + $HNO_3$ (red) and 50% $MAT^+dca^-$ + $HNO_3$ (blue) prior to ignition and b) Ignition delay of dicyanamide (DCA) based ionic liquids with $HNO_3$ based on rapid scan FTIR spectroscopy drop tests.*

Note that there appears to be a trend where ignition delay increases between 0-10% and 20-30% nanoparticle loading but decreases between 10-20%, perhaps indicating an optimal loading concentration for these nanoparticles between 10-20%. $MAT^+dca^-$ + Al had the fastest ignition delay time, and was consistently under 200 msec. Additional experiments are forthcoming.

**Temperature-jump thermal decomposition of cyano anion based ionic liquids**

In order to avoid polymerization reactions of the anions or alkylated anions in heating ILs, rapid heating to vaporize the thermal decomposition products prior to polymerization was performed using temperature-jump (T-jump) Fourier transform infrared spectroscopy. [2] Additional evidence for the $S_N2$ alkyl abstractions is seen in the T-jump experiment involving $BMIM^+SCN^-$, which in Figure 2a clearly shows the formation of $CH_3NCS$. For $BMIM^+SCN^-$, the intense peak at 2080 $cm^{-1}$ and smaller peak at ~2200 $cm^{-1}$ in Figure 2a suggests the formation of $SCN-CH_3$,[3] whereas $NCS-CH_3$ would have only a single peak at 2180 $cm^{-1}$,[4] and is consistent with the VUV-PI-TOFMS results for $BMIM^+SCN^-$. Additional evidence for $CH_3NCS$ formation is given by the m/z = 73 peak in the TGA-MS results. No HNCS or HSCN was detected. These experiments also indicate the demethylation of the imidazolium cation to form butylimidazole and a methylated anionic species for $BMIM^+TCM^-$ and $BMIM^+dca^-$ ILs that were not detected in the TGA-MS or VUV-PI-TOFMS experiments. The methylated dicyanamide (with two –CN groups) and methylated tricyanomethanide (three –CN groups) products likely polymerize when heated slowly, which would explain their absence in the VUV-TOFMS and TGA-MS experiments, while methylated thiocyanate (with only one –CN group) cannot polymerize. For $BMIM^+TCM^-$, Figures 2b and 2c demonstrate a good match from 2100 $cm^{-1}$ to 2300 $cm^{-1}$ with data from Finnerty et. al.[5] (used with permission), indicating methylation of the terminal nitrogen on the tricyanomethanide species, $CH_3$-$NCC(CN)_2$ rather than at the central carbon, $CH_3$-$C(CN)_3$. This is consistent with the M06 IR simulation in Figure 2e indicating that there should be no peaks in this region for the centrally methylated species. For $BMIM^+dca^-$ (Figure 2d), there are two peaks which arise from the methylated product at ~1600 $cm^{-1}$ and ~2200 $cm^{-1}$. From the M06 IR simulation (Figure 2f), both the terminally and centrally methylated dicyanamide species show peaks in the 2200 $cm^{-1}$ range, so the indentity of this product isn't clear. However, the simulated spectrum of the terminally methylated species shows a small peak at ~1600 $cm^{-1}$ whereas the centrally methylated dicyanamide simulation does not show any peaks in this region. Also, previous DFT calculations indicate that the barrier to form the terminally methylated dicyanamide should be lower than for the centrally methylated product.[6]

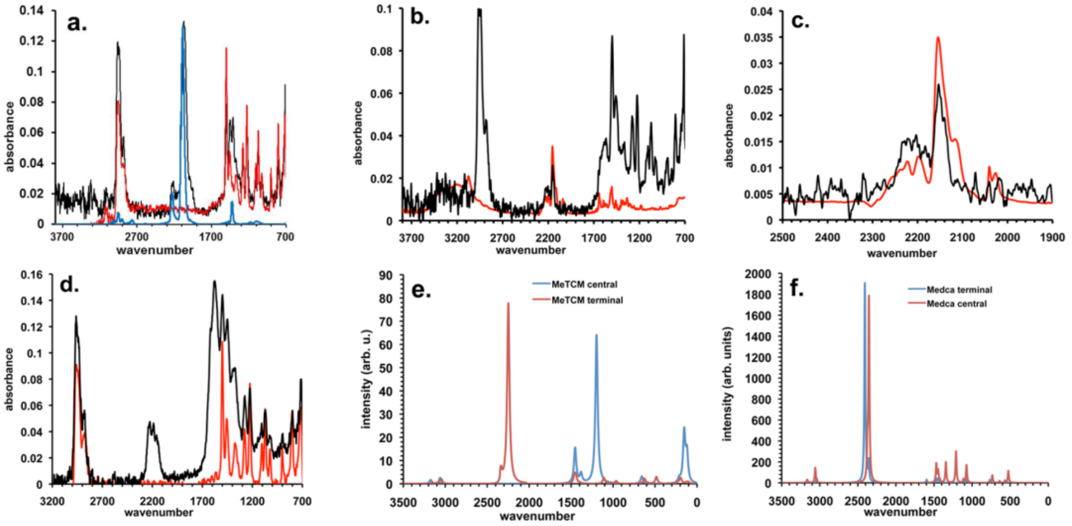


***Figure 2.*** *T-jump FTIR spectra of a) $BMIM^+SCN^-$ decomposition products (black) compared to a $H_3CNCS$ (blue, reference [3]) and 3:1 ratio of butylimidazole and methylimidazole (red), b) $BMIM^+TCM^-$ decomposition products (black) and linear ketenimine (red, from reference [5]), c) an expanded view of the central peak in (b), d) $BMIM^+dca^-$ decomposition products (black) and butylimidazole (red), e) DFT IR simulation of methylated $TCM^-$, and f) DFT IR simulation of methylated $dca^-$.*

### Ultrasonic spray approach to investigate hypergolic IL ignition delay times under different spray conditions

In order to investigate the heterogeneous chemistry of hypergolic ionic liquids, an experimental design for spraying ILs and oxidizers in a highly controlled manner was devised. ILs are difficult to make into sprays simply by forcing them through a nozzle using backing pressure. One successful way to spray ILs is by using an ultrasonic nozzle, as depicted in Figure 3a. The IL and the oxidizer droplet sizes, relative collision velocities and other parameters will be probed. The ultrasonic nozzles have been ordered and this experimental setup will be up and running in FY15.

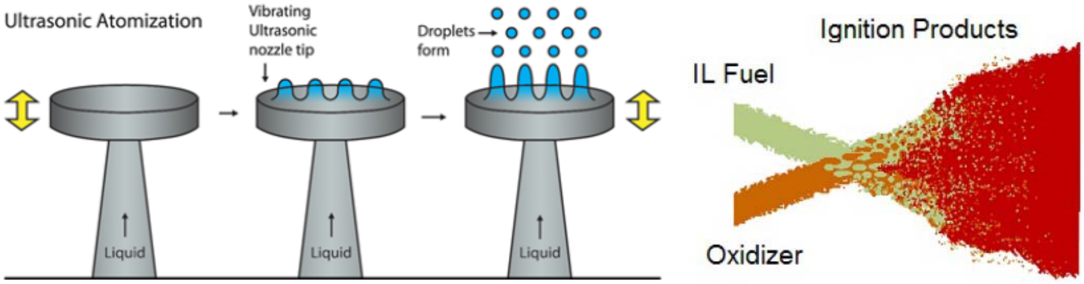


***Figure 3.*** *a) Illustration of ultrasonic atomization process, b) Illustration of setup to combine IL and oxidizer sprays.*

**Determination of ionic liquid vaporization and reaction mechanisms by tunable VUV spectroscopy**

Finalization of the experiments at the Advanced Light Source Chemical Dynamics Beamline investigating the thermal decomposition of hypergolic ILs has been achieved, and the results have been submitted for publication to the Journal of Physical Chemistry A. Due to the unusually high heats of vaporization of room-temperature ionic liquids (RTILs), volatilization of RTILs through thermal decomposition and vaporization of the decomposition products can be significant. Upon heating of cyano-functionalized anionic RTILs in vacuum, their gaseous products were detected experimentally via tunable vacuum ultraviolet photoionization mass spectrometry performed at the Chemical Dynamics Beamline 9.0.2 at the Advanced Light Source.

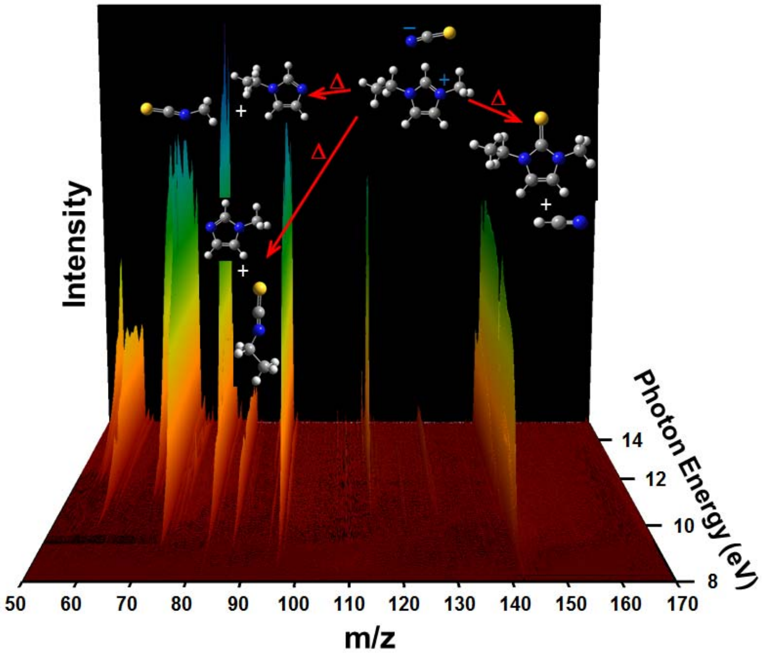


***Figure 4.*** *Thermal decomposition mechanisms of EMIM$^+$SCN$^-$ determined by tunable VUV PI-TOFMS.*

Experimental evidence for di- and tri-alkylimidazolium cations and cyano-functionalized anionic RTILs confirms thermal decomposition occurs primarily through two pathways: deprotonation of the cation by the anion, and dealkylation of the imidazolium cation by the anion. Secondary reactions include possible cyclization of the cation and C2 substitution on the imidazolium, and their proposed reaction mechanisms are introduced in the journal submission. Additional evidence supporting these mechanisms was obtained using thermal gravimetric analysis/mass spectrometry, gas chromatography/mass spectrometry and temperature-jump infrared spectroscopy. In order to predict the overall thermal stability in these ionic liquids, the ability to accurately calculate both the basicity of the anions and their nucleophilicity in the ionic liquid is critical. Both gas phase and condensed phase (generic ionic liquid (GIL) model) density functional theory calculations support the decomposition mechanisms and the GIL model could provide a highly accurate means to determine thermal stabilities for ionic liquids in general.

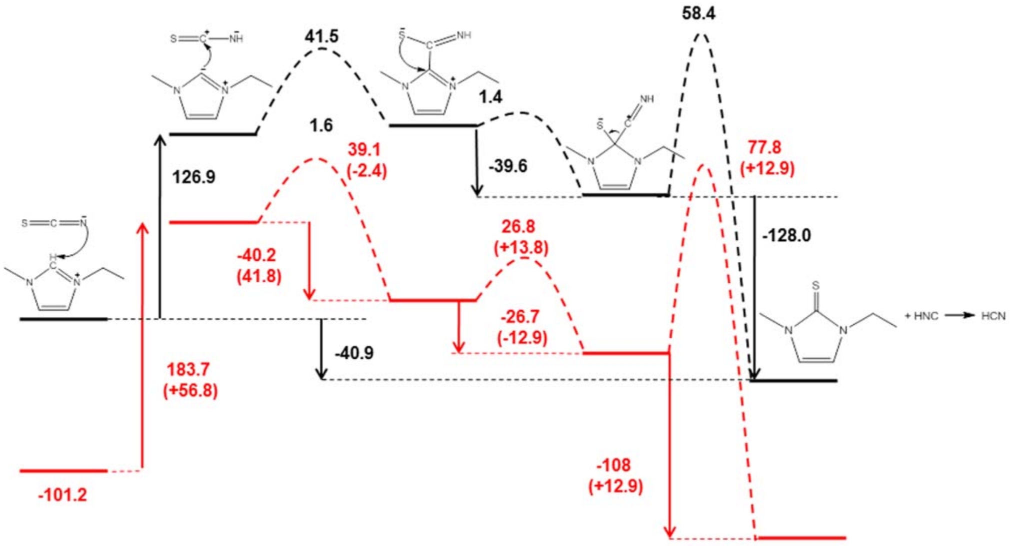
In the calculations of the free energy of acidity of the protonated anions ($\Delta G_{acid}$, Table 1), the order of acidity changes between the gas phase and the simulated consendsed phase (SMD-GIL) of the nitrate and the dicyanamide species, which could explain why proton transfer between $HNO_3$ and dca$^-$ is rapid in the ionic liquid condensed phase: In the gas phase calculations, the higher value of $\Delta G_{acid}$ for $HNO_3$ would favor a proton remaining bonded to the nitrate anion, while in the SMD-GIL condensed phase calculations, the higher value of $\Delta G_{acid}$ for Hdca indicates that the proton would be transferred from the $HNO_3$ to the dca$^-$ anion. Proton transfer from $HNO_3$ to dca$^-$ has been proposed previously as the first step in the hypergolic ignition of dca$^-$ based ILs.[7]

**Table 1.** Calculated free energies of acidity, $\Delta G_{acid}$, in the gas phase and in the condensed phase by SMD-GIL and SMD (water) at the M06/6-31+G(d,p) level of theory.

| acid | $\Delta G_{acid}$ (g) (kJ/mol) | | $\Delta G_{acid}$ (l) SMD-GIL (kJ/mol) | | $\Delta G_{acid}$ (l) SMD-$H_2O$ (kJ/mol) |
|---|---|---|---|---|---|
| HNCS | 1332.5 | HNCS | 607.0 | HNCS | 549.5 |
| $HNO_3$ | 1306.7 | HNCNCN | 578.0 | HNCNCN | 521.8 |
| HSCN | 1274.2 | $HNO_3$ | 566.6 | Hvdca 04 | 515.2 |
| HNCNCN | 1272.6 | Hvdca 01 | 565.2 | Hvdca 01 | 514.6 |
| NCNHCN | 1234.6 | Hvdca 04 | 564.9 | NCNHCN | 495.9 |
| Hvdca 01 | 1212.1 | NCNHCN | 550.3 | $HNO_3$ | 494.9 |
| Hvdca 04 | 1203.3 | HSCN | 548.8 | HSCN | 492.6 |
| HTCM (central) | 1197.1 | HTCM (central) | 537.9 | HTCM (central) | 490.5 |
| HTCM (terminal) | 1188.7 | HTCM (terminal) | 533.9 | HTCM (terminal) | 483.9 |
| Hvdca 02 | 1152.7 | Hvdca 03 | 518.1 | Hvdca 03 | 471.4 |
| Hvdca 03 | 1146.1 | Hvdca 02 | 517.6 | Hvdca 02 | 468.6 |

Hvdca 01 = terminal NH, Hvdca 02 = $-CCN_1H$, Hvdca 03 = $-CCN_2H$, Hvdca 04 = central NH

Another interesting feature discovered using the SMD-GIL method was the increase in activation energy for proton transfer in EMIM+SCN- in going from the gas phase to the condensed phase (Figure 5). This effect can be explained by the larger stabilizing effect of solvation on the ion pair reactant than on the less charge-separated structure in the transition state, evidenced in the black versus red arrows on the left hand side of Figure 5 which shows an increase of 56.8 kJ/mol in the activation barrier in going form the gas phase to the condensed phase.



$EMIM^+SCN^- \rightarrow EIM + MeNCS$, $\Delta G^\ddagger = 148.9$ (160.0)
$EMIM^+SCN^- \rightarrow MIM + EtNCS$, $\Delta G^\ddagger = 143.0$ (166.5)

***Figure 5.*** *Free energy reaction profile comparison of gas phase (black) and SMD-GIL (red) using M06/6-31+G(d,p) for the formation of m/z 142 from EMIM$^+$SCN$^-$. Values are in kJ/mol.*

## IL ion pair dipole measurement from He nanodroplet FTIR in a Stark field

In collaboration with Professor Gary Douberly, FTIR spectroscopy experiments were performed on single IL ion pairs in helium nanodroplets (Figure 6), and this work was published in the Journal pf Physical Chemistry A.[8] This work measured the FTIR spectra of EMIM+NTf$_2$- in zero (Figure 7) and high electric fields, and the permanent dipole of the ion pair was determined to be 10.8 D (Figure 8). To our knowledge, this is the first experimental determination of the dipole moment of a single IL ion pair.

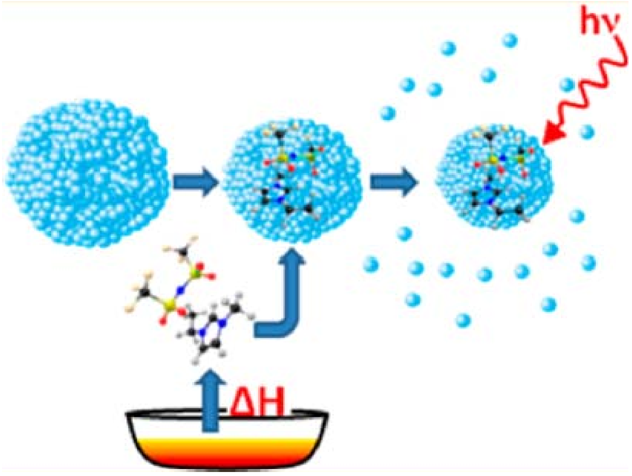


***Figure 6.*** *Illustration of He nanodroplet pickup of EMIM+NTf2- and IR absorption.*

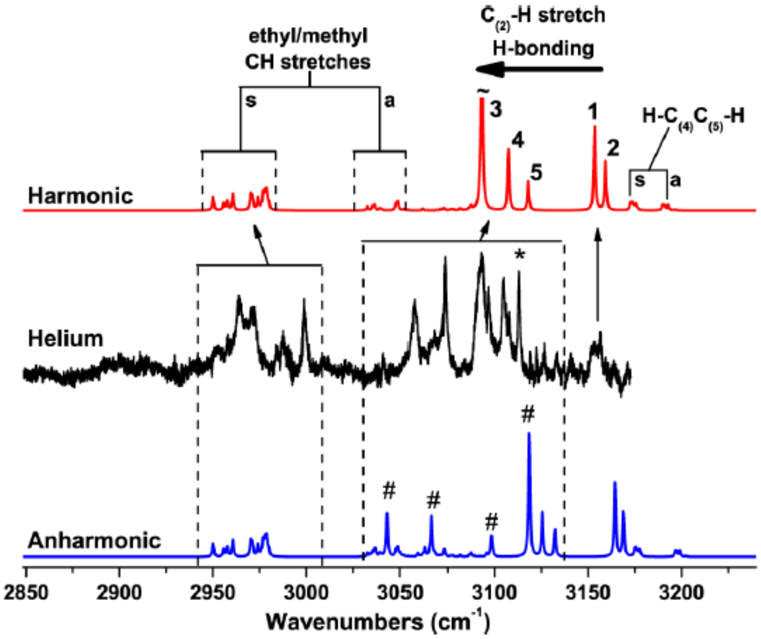


***Figure 7.*** *Experimental and calculated infrared spectra of EMIM$^+$NTf$_2^-$.*

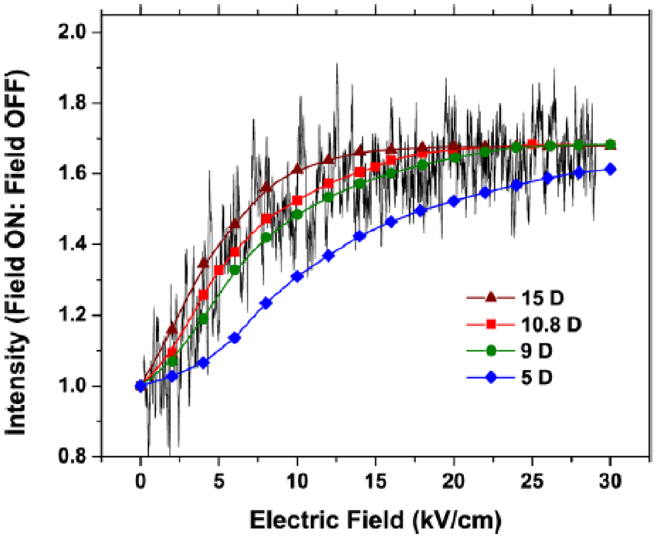


***Figure 8.*** *Experimental determination of the permanent dipole moment of EMIM$^+$NTf$_2^-$.*

## Determination of ionic liquid hypergolic ignition delay model parameters and reaction pathways via chemical kinetics measurements and molecular dynamics simulations.

### Kinetics of the elementary reaction $NO_2$ + $N_2H_3$

In the process of developing and building a chemical kinetics model, sometimes hundreds of chemical species and thousands of elementary reactions can be considered. Often, these elementary reactions are difficult to probe due to their extremely fast rates of reaction. One important reaction in the chemical kinetics model for hypergolic ignition is $NO_2 + N_2H_3 \rightarrow HONO + N_2H_2$. We have successfully measured the rate of this reaction at several $NO_2$ concentrations using a laser photolysis flow tube reactor coupled to a mass spectrometer (Figure 9). This work, along with accompanying *ab initio* and kinetics calculation analyses will be submitted for publication shortly.

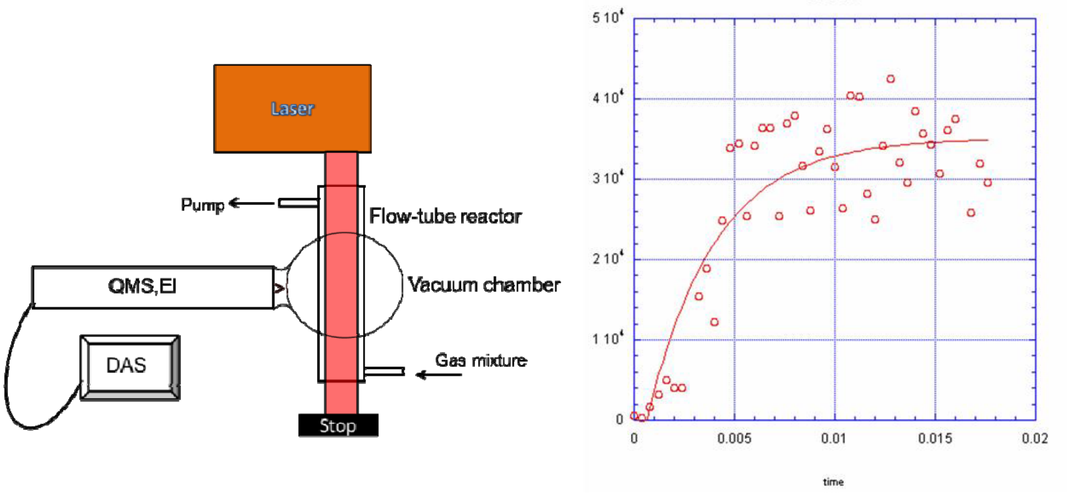


***Figure 9.*** *Experimental setup for the kinetics flow tube reactor and the formation of HONO.*

**Molecular dynamics (MD) investigation of 1,5-dinitrobiuret**

In collaboration with Professor Bill Hase, molecular dynamics on the reactivity of 1,5-dinitrobiuret (DNB) were carried out in order to differentiate between thermal decomposition[9] and chemical reactivity by initiating the MD trajectories as a hydrogen addition to (dehydrogenated) N3.[10] Trajectory analysis and subsequent, higher-level stationary point calculations resulted in the energy profile seen in Figure 10. While the mechanism determined in this work is similar to the previous one,[9] the product energy distributions are significantly different due to the differences in initial trajectory conditions, where this work shows inverted rovibrational product distributions, whereas the previous work showed thermal rovibrational distributions.

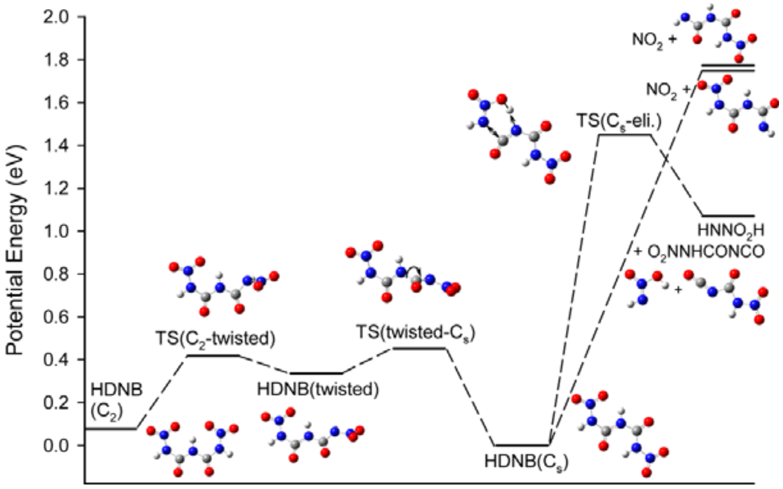


***Figure 10.*** *Reaction energetics profile for the decomposition mechanisms of DNB.*

### Desorption Electrospray investigation 2-hydroxyethylhydrazinium nitrate components

In collaboration with Professor Dick Zare, experimental investigation of the catalytic reactivity of 2-hydroxyethylhydrazinium nitrate ionic liquid using desorption electrospray ionization mass spectrometry was carried out. Data analysis and interpretation is ongoing. Preliminary results indicate that sodiated molecular impurities exist in the HEHN IL and in the molecular precursor (Figure 11):

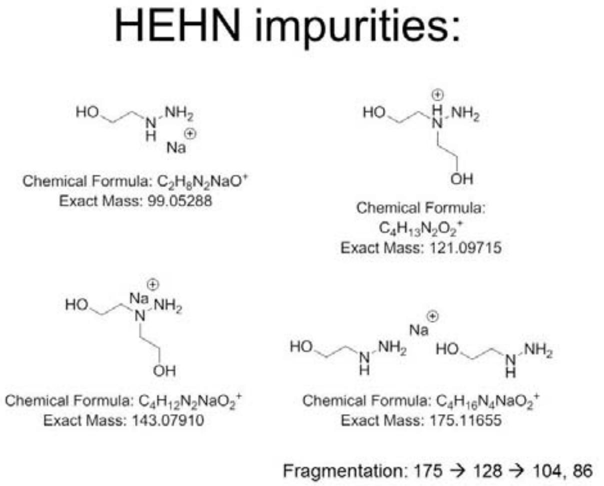


**Figure 11.** *Impurities identified in HEHN using high-resolution DESI-MS.*

## 2.2.4 REFERENCES TASK II

1 Perez, J. P. L.; McMahon, B. W.; Anderson, S. L. *J. Prop. Power*, **2013**, *29*, 489-494.
2 Brill, T. B.; Brush, P. J.; James, K. J.; Shepherd, J. E.; Pfeiffer, K. J. *Appl. Spect.*, **1992**, *46*, 900-911.
3 Johnson, T. J.; Sams, R. L.; Sharpe, S. W. In *Proc. SPIE 5269 Chemical and Biological Point Sensors for Homeland Defense* Providence, RI, 2004; Vol. 5269, p 159-167.
4 Stein, S. E. Gaithersburg, MD, 2014.
5 Finnerty, J.; Mitschke, U.; Wentrup, C. *J. Org. Chem.*, **2002**, *67*, 1084-1092.
6 Kroon, M. C.; Buijs, W.; Peters, C. J.; Witkamp, G.-J. *Thermochim. Acta*, **2007**, *465*, 40-47.
7 Chambreau, S. D.; Schneider, S.; Rosander, M.; Hawkins, T.; Gallegos, C. J.; Pastewait, M. F.; Vaghjiani, G. L. *J. Phys. Chem. A*, **2008**, *112*, 7816-7824.
8 Obi, E. I.; Leavitt, C. M.; Raston, P. L.; Moradi, C. P.; Flynn, S. D.; Vaghjiani, G. L.; Boatz, J. A.; Chambreau, S. D.; Douberly, G. E. *J. Phys. Chem. A*, **2013**, *117*, 9047-9056.
9 Liu, J.; Chambreau, S. D.; Vaghjiani, G. L. *J. Phys. Chem. A*, **2011**, *115*, 8064-8072.
10 Sun, R.; Siebert, M. R.; Xu, L.; Chambreau, S. D.; Vaghjiani, G. L.; Lischka, H.; Liu, J.; Hase, W. L. *J. Phys. Chem. A*, **2014**, *118*, 2228-2236.

## 3.0 FUTURE RESEARCH RECOMMENDATIONS:

### 3.1 TASK I.

The isolation and characterization of a new triply charged aluminum anion with a rare coordination number of six holds the promise that other new anions can be made, using for example the cyanide or dicyanamide anion which provide multiple coordination sites. Those type of anions could increase the overall hydrogen content of the anion and lead to a new class of energetic hydrogen-rich materials.

The discovery of a new simple route to analytically pure heterocyclic borohydride salts, opens the door to a new class of ILs with heterocyclic cations and the complexed $[Al(BH_4)_4]^-$ anion. Furthermore, the chemistry of alkaline-metal amine complexes should be further exploited as these may hold the potential for novel synthetic approaches to otherwise only with difficulty obtainable materials.

Higher level simulations will be required to guide and prioritize the developing synthetic and experimental investigations. The initial issues that are germane to the objectives include:

1. How does the reactivity of hydrogen peroxide compare with that of water?
2. What are the analogous energetics of the more highly reactive neutral aluminum borohydrides? Are qualitatively different reactions possible in this less coordinatively saturated system?
3. Can calculations explain the inertness of many of these systems to analogous reaction with ammonia and amines?
4. What are the energetics of thermal degradation of ether and amine ABH complexes?
5. Which substituents stabilize these systems to hydrolysis and what effect does functionalization have on hypergolic reactivity?

### 3.2 TASK II.

In FY 15, the Ionic Liquids Ignition Group plans to complete the nanoparticle-infused ionic liquid hypergol testing and to initiate the ultrasonic ionic liquid spray investigation into heterogeneous processes in hypergolic ignition of ILs. We also plan to continue collaborations involving the DESI-MS mechanistic investigations and the ALS investigations. Preparation of publications include the chemical kinetics investigation of $NO_2 + N_2H_3$, oxidation kinetics of IL aerosols, chemical kinetics modeling of AF-315E, and the catalytic reactivity of ionic liquid aerosols.

## 4.0 Appendix A: In-house Activities

**Personnel:**
**Air Force Civilian:**
J. D. Mills, Ph.D, Chemist (50%)
G. L. Vaghjiani, Ph.D, Chemist (20%)
S. Schneider, Ph.D, Chemist (70%)
S. Deplazes, Ph.D, Chemist (90%)
J. Boatz, Ph.D Chemist (10%)

**On-site Contractor:**
Yonis Ahmed, Ph.D., Chemist (100%)
S. D. Chambreau, Ph.D., Chemist (100%)
C. Gibson, B.Sc., Chemist (100%)

**Air Force Military:**
Lt. A. Sheppard, B.Sc., Aerospace Eng. (30%)
Capt. A. Beauchamp, M.Sc., Chemist (50%)
Lt. T. Schulmeister, B.Sc., Physics. (30%)

## 5.0 Publications:

### Published in Peer Reviewed Journals, Books, etc:

1) "Helium Nanodroplet Isolation and Infrared Spectroscopy of the Isolated Ion-Pair 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide" Emmanuel I. Obi, Christopher M. Leavitt, Paul L. Raston, Christopher P. Moradi, Steven D. Flynn, Ghanshyam L. Vaghjiani, Jerry A. Boatz, Steven D. Chambreau, and Gary E. Douberly, *J. Phys. Chem. A*, **2013**, 117 (37), 9047–9056.
2) "Direct Dynamics Simulation of the Activation and Dissociation of the Ionic Liquid 1,5-Dinitrobiuret (DNB)" Rui Sun, Matthew R Siebert, Lai Xu, Steven D. Chambreau, Ghanshyam L. Vaghjiani, Hans Lischka, Jianbo Liu, and William Louis Hase, *Journal of Physical Chemistry A* **2014** DOI: 10.1021/jp5002622
3) "Boron Nanoparticles with High Hydrogen Loading: Mechanism for B–H Binding and Potential for Improved Combustibility and Specific Impulse" Jesus Paulo L. Perez, Brandon W. McMahon, Jiang Yu, Stefan Schneider, Jerry A. Boatz, Tom W. Hawkins, Parker D. McCrary, Luis A. Flores, Robin D. Rogers, Scott L. Anderson, *Appl. Mater. Interfaces*, **2014**, *6* (11), 8513–8525.

### Accepted/Submitted for Publication:

1) "Dynamics Simulations and Statistical Modeling of Thermal Decomposition of 1-Ethyl-3-methylimidazolium Dicyanamide and 1-Ethyl-2,3-dimethylimidazolium Dicyanamide" Jianbo Liu, Steven D. Chambreau, Ghanshyam L. Vaghjiani,. *Journal of Physical Chemistry A*, **2014**, Accepted. DOI: 10.1021/jp5095849

### Invention Disclosures and Patents Granted:

1) "Catalytic hypergolic bipropellants" Schneider, Stefan; Hawkins, Tommy W.; Ahmed, Yonis; Rosander, Michael U.S. (2014), US 8758531
   Provided is a fuel of catalytic metal-contg. ionic liq. (MCIL) and an IL, to spur hypergolic ignition of such liqs. upon contact with an oxidizer to define a hypergolic bipropellant.
2) "Bipropellants based on chosen salts" Schneider, Stefan; Hawkins, Tommy W.; Ahmed, Yonis; Rosander, Michael U.S. (2014), US 8758531
   Advanced bipropellant fuels with fast ignition upon mixing with storable oxidizer (N204 , nitric acid) have been synthesized and demonstrated. The bipropellant fuels are based upon salts containing dicyanamide or tricyanomethanide anions and employ at least two hydrazine functionalities in the cations.

### Invited Lectures, Presentations, Talks, etc:

"Recent advances in understanding the reactivity of energetic ionic liquids in propulsion applications" Steven D. Chambreau, Ghanshyam L. Vaghjiani, Timothy K. Minton, Stephen R. Leone, poster presented at Air Force Office of

Scientific Research Molecular Dynamics Contractors review meeting, Arlington, VA, May 19, 2014.

“Advances in Understanding the Ignition of Ionic Liquid Propellants” Steven D. Chambreau, invited presentation at 6.1 Review, Antelope Valley College, January 28, 2014.

“Recent advances in understanding the reactivity of energetic ionic liquids in propulsion applications” Steven D. Chambreau, Ghanshyam L. Vaghjiani, Timothy K. Minton, Stephen R. Leone, talk presented at the American Chemical Society Annual Fall Meeting, San Francisco, CA, August 12, 2014.

“Synthesis of novel hydrazine tethered ionic liquids” Beauchamp, Andrew; Deplazes, Stephan; Ahmed, Yonis; Franquera, Christina; Schneider, Stefan, presented at 248th ACS National Meeting & Exposition, San Francisco, CA, United States, August 10-14, 2014.

“Synthesis and characterization of 5-(hydrazino-alkly) tetrazoles” Ahmed, Yonis; Beauchamp, Andrew; Deplazes, Stephan; Franquera, Christina; Schneider, Stefan, presented at 248th ACS National Meeting & Exposition, San Francisco, CA, United States, August 10-14, 2014.

“Catalytic ignition of ionic liquid fuels by ionic liquids” Schneider, Stefan; Deplazes, Stephan; Ahmed, Yonis; Beauchamp, Andrew; Franquera, Christina, presented at 248th ACS National Meeting & Exposition, San Francisco, CA, United States, August 10-14, 2014.

“Novel coordination chemistry of aluminum borohdyride” Deplazes, Stephan; Schneider, Stefan; Ahmed, Yonis; Franquera, Christina; Beauchamp, Andrew, presented at 248th ACS National Meeting & Exposition, San Francisco, CA, United States, August 10-14, 2014.

## Honors Received (include lifetime honors such as Fellow, Honorary Doctorates, etc:

Dr. Schneider was bestowed the competitive **General Benjamin D. Foulois Award**. This award is given for significant and outstanding in-house science of importance to the Air Force. This award recognizes a culmination, multi-year outstanding achievement. Air Force Research Laboratory, Edwards AFB, CA, Jan 2014.

## Extended Scientific Visits From and To Other Laboratories:

Dr. Chambreau traveled to Berkeley, CA to perform experiments at the Chemical Dynamics Beamline at the Advanced Light Source (Lawrence Berkeley National Laboratory), December 3-11, 2013.

Dr. Chambreau traveled to Stanford University to perform experiments using desorption electrospray ionization mass spectrometry to investigate the catalytic reactivity of ionic liquid monopropellants: August 14-19, 2014.

Dr. Chambreau traveled to the Advanced Light Source at Lawrence Berkeley National Laboratory to perform ongoing experiments using tunable vacuum ultraviolet photoionization time of flight spectrometry to probe the catalytic reactivity of aerosolized ionic liquid monopropellants, August 19-26, 2014.

## 6.0 Appendix B: Technology Assists, Transitions, or Transfers

| Task Title | Performance Period | AFOSR Program Manager | TD Performer | Customer | Research Result | Application | From | To | Ap |
|---|---|---|---|---|---|---|---|---|---|
| **IONIC LIQUID-BASED<br>PROPELLANTS** | 10/2010-9/2013 | BERMAN | USAF-AFRL JON 33SP084D, Brand | DoD | Scale-up novel ionic liquid propellants based on AFOSR research results that yield high performance liquid chemical propulsion. | Advanced Liquid Rocket Engines | L | AF | Pd |
| **IONIC LIQUID-BASED<br>PROPELLANTS** | 10/2012-9/2015 | BERMAN | USAF-AFRL Brand | NASA | Providing advanced monopropellant based on AFOSR material for spacecraft demonstration | Spacecraft Monopropulsion | L,I | O | Pd |
| **IONIC LIQUID-BASED<br>PROPELLANTS** | 6/2012-12/2014 | BERMAN | USAF-AFRL Brand | Aerojet | Providing advanced monopropellants based on AFOSR material for ACS demonstration | Attitude control for missiles | L | I | Pd |
| **IONIC LIQUID-BASED<br>PROPELLANTS** | 10/2010-9/2013 | BERMAN | USAF-AFRL (CFD RESEARCH CORP., HUNTSVILLE, AL, Contract FA9300-11-C-3004), Vaghjiani | DoD | Development of software for prediction of ignition delays for energetic ionic liquids. Phase-II stage of development.<br>Also, making energetic IL propellants that complement AFOSR efforts. | Advanced Liquid Rocket Engines | L | I | Pd |
| **IONIC LIQUID-BASED<br>PROPELLANTS** | 10/2010-9/2013 | BERMAN | USAF-AFRL (WASATCH MOLECULAR INC., SALT LAKE CITY, UT, Contract FA9300-11-C-3012),Vaghjiani | DoD | Development of software for prediction of ignition delays for energetic ionic liquids. Phase-II stage of development.<br>Complements AFOSR & EOARD IL ignition M&S efforts. | Advanced Liquid Rocket Engines | L | I | Pd |
| **IONIC LIQUID-BASED<br>PROPELLANTS** | 8/2012-8/2014 | BERMAN | USAF-AFRL (ULTRAMET, PACOIMA, CA Contract FA9300-12-C-xxxx),Vaghjiani & Zuttarelli | DoD | Modeling the decomposition of HAN-based monopropellants and associated catalysts. Phase-II stage of development.<br>Complements AFOSR energetic IL propellant decomposition efforts. | Advanced Liquid Rocket Engines | L | I | Pd |

**Note: In each of the last three columns, enter the appropriate codes from the lists below:**

**Transitioned From: AFRL = L; Industry = I; Academia = A**

**Transitioned To: Industry = I; Air Force 6.2 or 6.3 = AF; Other AF, DoD, Government, etc. = O (please specify)**

**Application: Product (New or Improved) Process (New or Improved) = Pc; Other = O (please specify)**