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14. ABSTRACT Although molten salts, more recently known as ionic liquids (ILs), have been known for almost a century (for instance, ethylammonium nitrate, mp =12 °C, was discovered in 1914), the rapid development of ionic liquid chemistry has only occurred within the last decade. In 2000, only 217 papers were published on the subject, whereas in 2010, over 6,000 papers appeared in the literature. The number of possible ILs has been estimated at 10¹⁸. Detailed studies of ILs offer insight into new and more complex fundamental chemistry, as well as allow for an assessment for their potential application in emerging technologies such as in solar cells, fuel electrolytes, bio- or nano-catalysts, high-energy-density propellants, and green solvents. In order to better understand the volatilization process for ILs, the vapor evolved from heating the ionic liquid 1-ethyl-3-methylimidazolium bromide (EMIM+Br-) was analyzed via tunable vacuum ultraviolet photoionization time of flight mass spectrometry (VUV-PI-TOFMS) and thermal gravimetric analysis mass spectrometry (TGA-MS). For this ionic liquid, the experimental results indicate that vaporization takes place via the evolution of alkyl bromides and alkylimidazoles, presumably through alkyl abstraction via an S_N2 type mechanism, and that vaporization of intact ion pairs or the formation of carbenes is negligible. Activation enthalpies for the formation of the methyl and ethyl bromides were evaluated experimentally, H_‡(CH₃Br) = 116.1±6.6 kJ/mol and H_‡(CH₃CH₂Br) = 122.9±7.2 kJ/mol, and the results are found to be in agreement with calculated values for the S_N2 reactions. Comparisons of product photoionization efficiency (PIE) curves with literature data are in good agreement, and <i>ab initio</i> thermodynamics calculations are presented as further evidence for the proposed thermal decomposition mechanism. Estimates for the enthalpy of vaporization of 1-ethyl-3-methylimidazolium bromide and, by comparison, 1-butyl-3-methylimidazolium bromide (BMIM+Br-) from molecular dynamics calculations and their gas phase enthalpies of formation obtained by G4 calculations yield estimates for the ionic liquids, enthalpies of formation in the liquid phase: H_{vap}(298 K) (EMIM+Br-) = 168±20 kJ/mol, H_f, gas(298 K) (EMIM+Br-) = 38.4±10 kJ/mol, H_f, liq(298 K) (EMIM+Br-) = -130±22 kJ/mol, H_f, gas(298 K) (BMIM+Br-) = -5.6±10 kJ/mol, and H_f, liq(298 K) (BMIM+Br-) = -180±20 kJ/mol.					
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Volatilization Mechanism of 1-Ethyl-3-methylimidazolium Bromide Ionic Liquid



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Motivation to Study Room Temperature Ionic Liquids

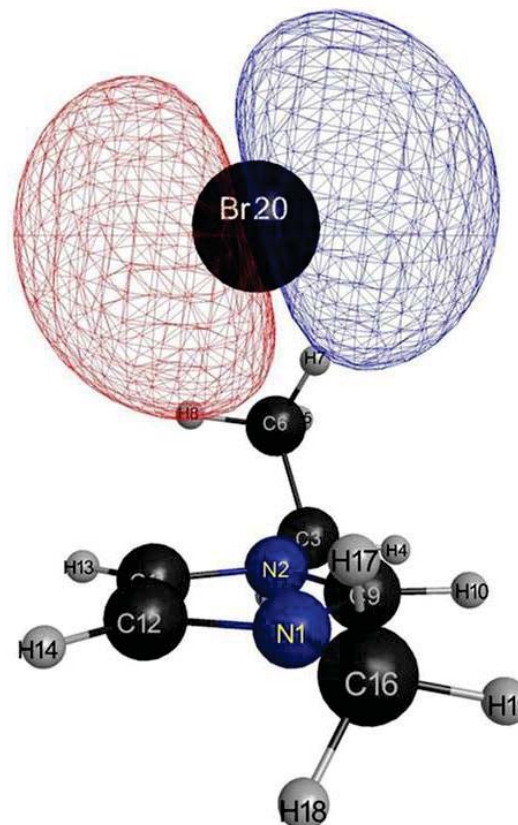


☐ Molten Salts @ RT

- ☐ Low mp
- ☐ Large (organic) ions
- ☐ Low volatility ($vp_{298\text{ K}} \ll 1\text{ Pa}$)
- ☐ Thermally stable
- ☐ Good conductivity
- ☐ Good solvents

☐ Unique reactivity

☐ Popularized in green/sustainable chemistry applications



☐ $> 10^{18}$ cation/anion pair combinations

☐ Enormous tunability



Hypergolic Ignition



- ❑ Autoignition at ambient P & T

- ❑ MMH/NTO current hypergol propellants

- ❑ IL hypergol fuels low vapor toxicity

- ❑ Operational cost savings (cf MMH)

- ❑ Higher performing than MMH

- ❑ Synthesis tunability

- ❑ T_b (calculated) $\gg T_d$ for ILs

- ❑ What role does decomposition/vaporization play in understanding IL/ox autoignition?

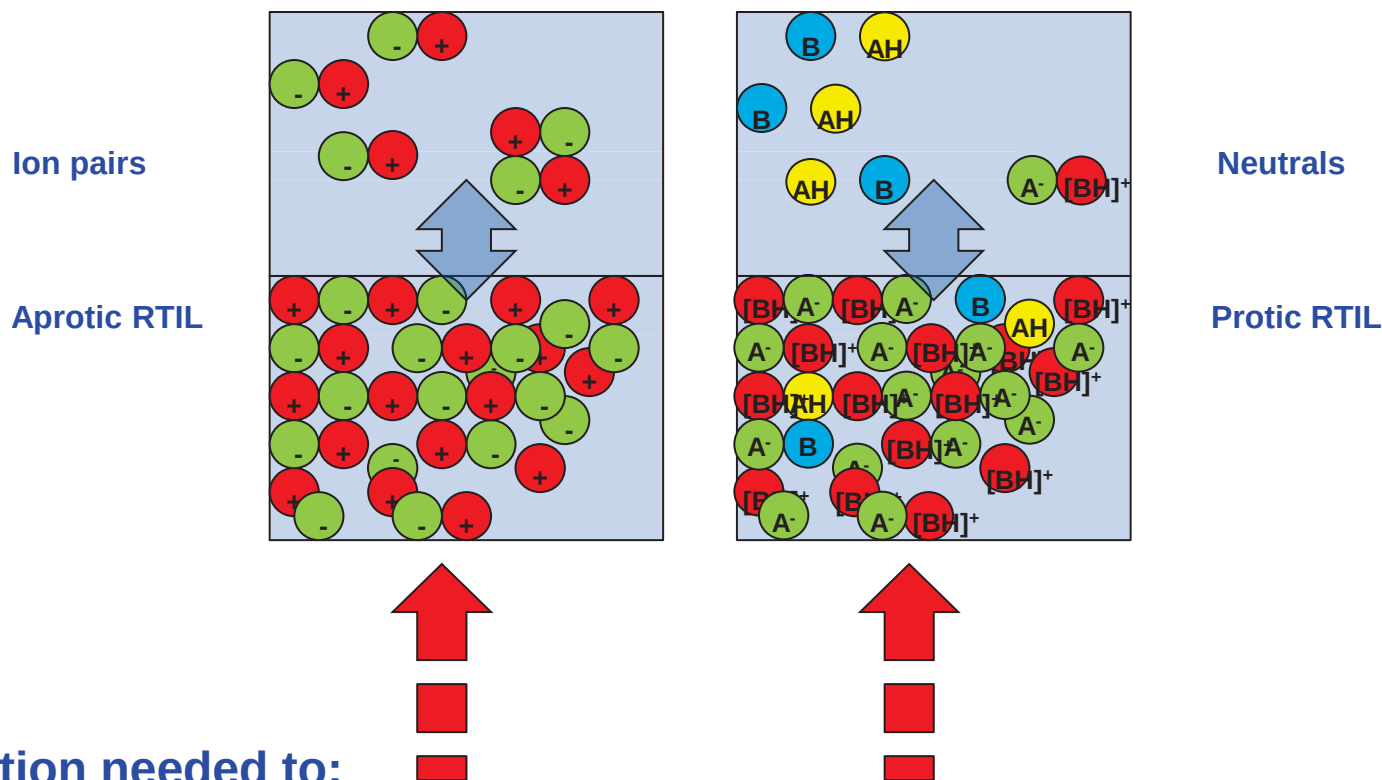


JPC-A 2008, 112, 7816





How Do ILs Volatilize?



Information needed to:

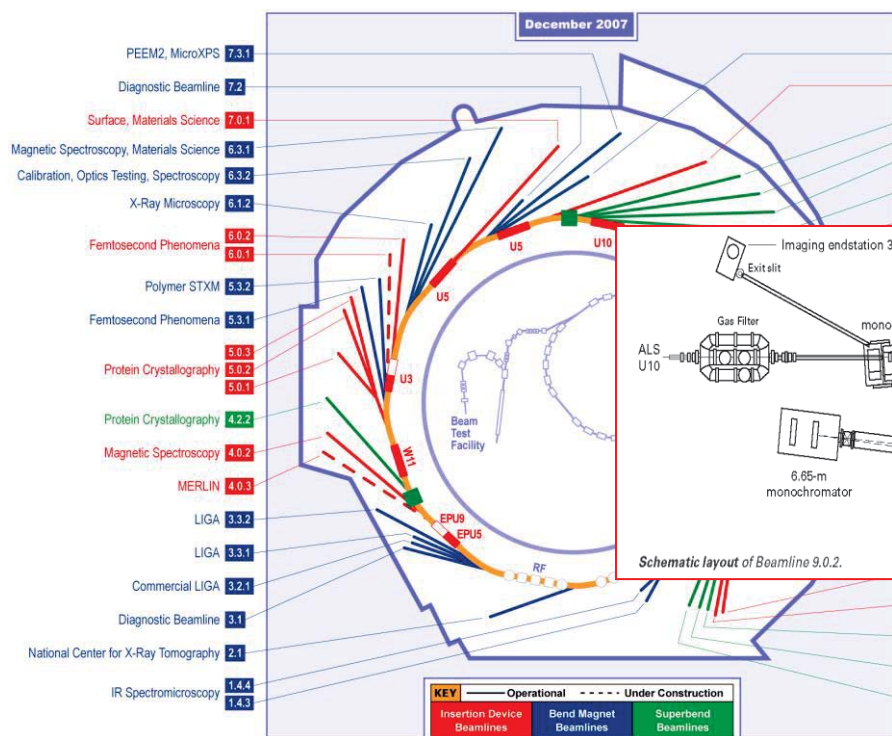
- ☐ Understand gas phase structure of ILs
- ☐ Determine heat of vaporization..... calibrate MD simulations
- ☐ (for $\Delta H_{f(l)}$ and therefore I_{sp})
- ☐ Characterize thermal decomposition of ILs
(basicity & nucleophilicity of anion)



Probing Ionic Liquid Vapor by VUV Photoionization Mass Spectrometry

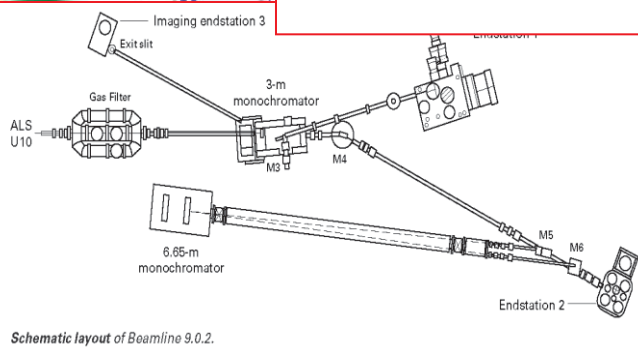
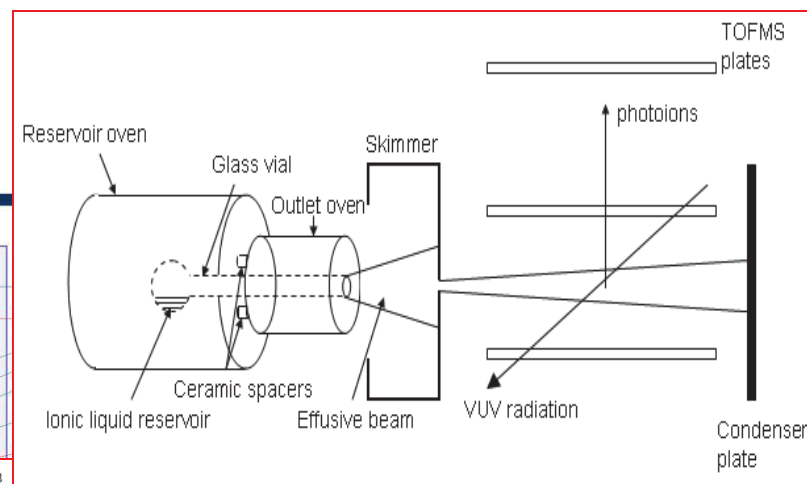


Beamlines at the ALS



Effusive Vapor Source

Separate temperature control of reservoir and outlet



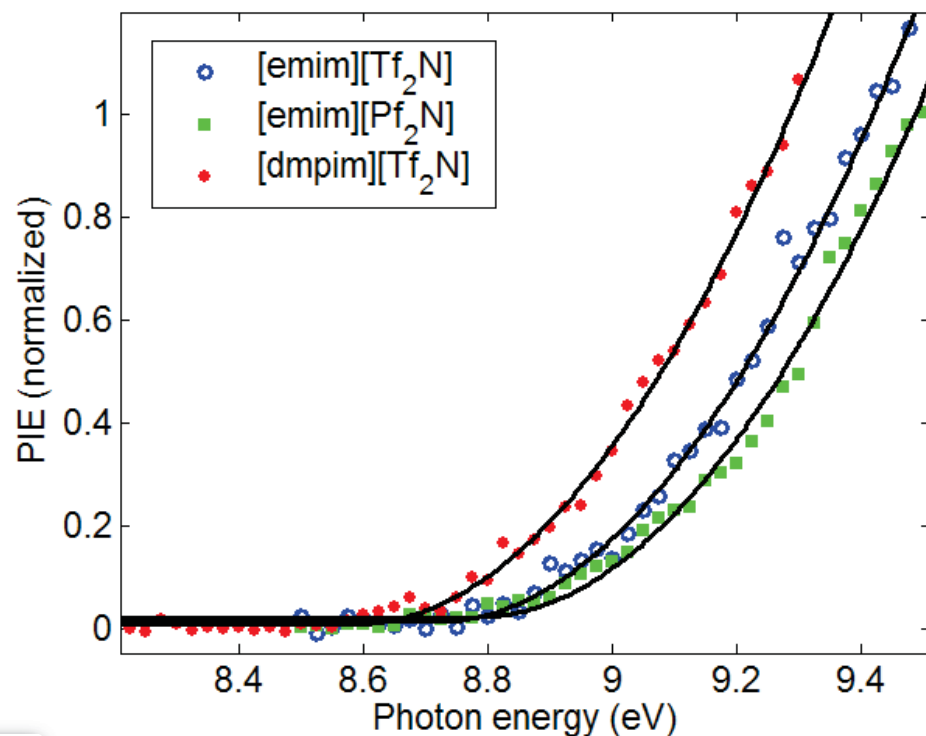
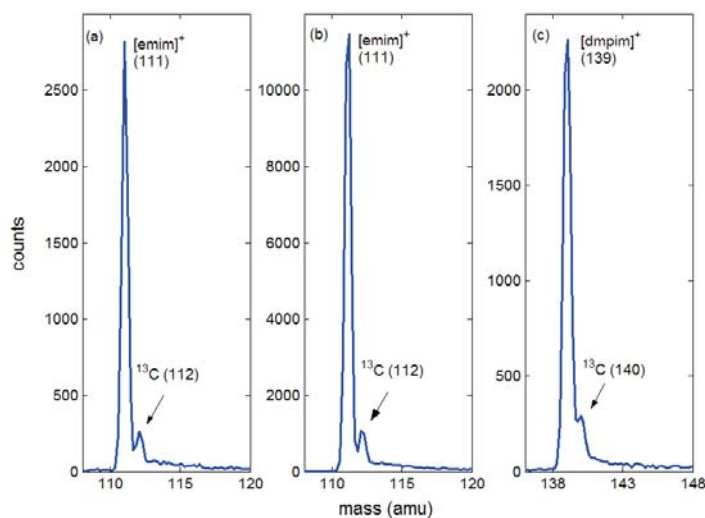
7.4-15.0 eV photons, 0.025 eV resolution, 0.040 eV absolute accuracy



Structure of Aprotic ILs in the Gas Phase



- PIE curves and structures



- Dissociative photoionization



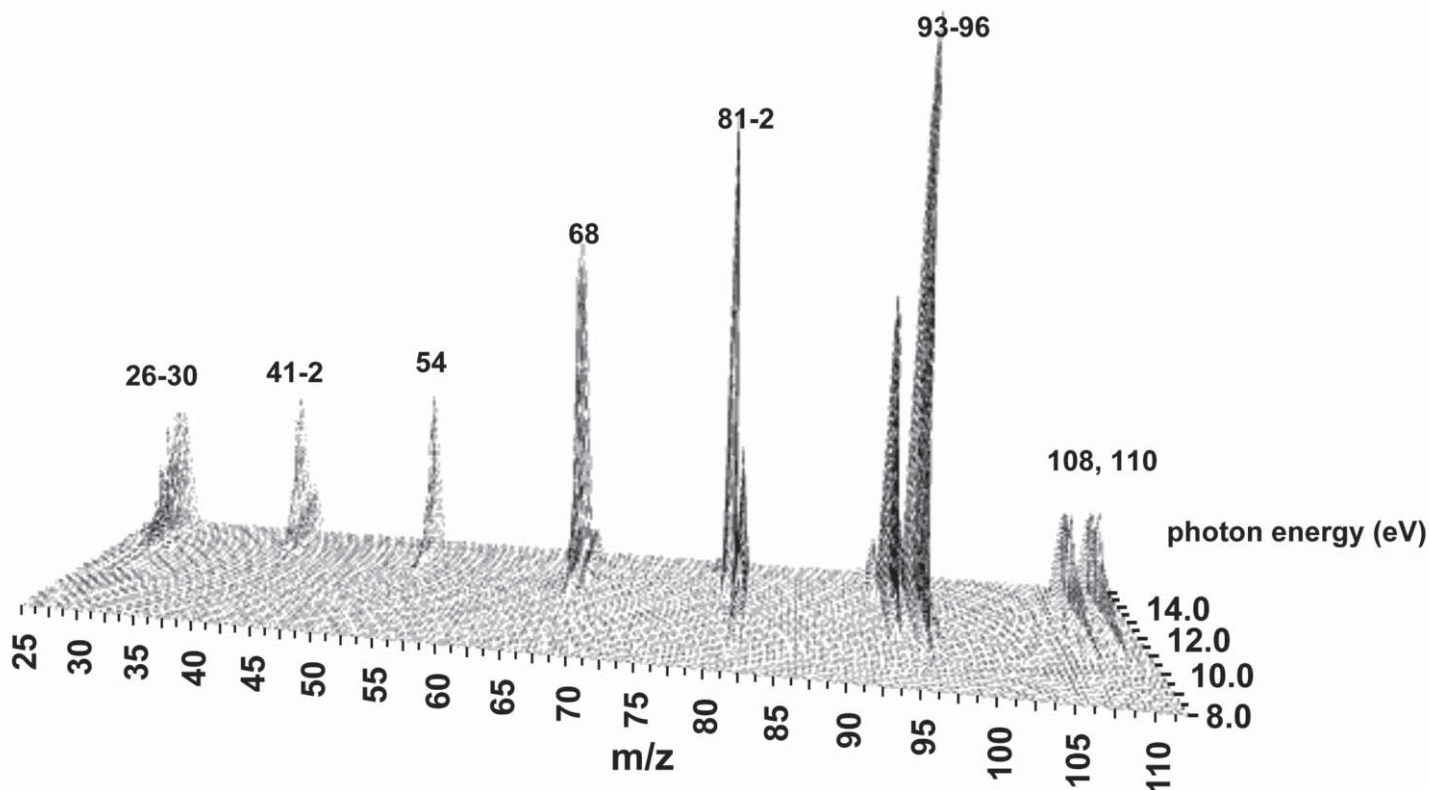
Appearance energies are:

[emim][Tf ₂ N]:	8.72 ± 0.03 eV
[emim][Pf ₂ N]:	8.78 ± 0.04 eV
[dmpim][Tf ₂ N]:	8.59 ± 0.03 eV

JPC-A 2010, 114, 879



Volatilization of EMIM⁺Br⁻



☐ No ion signal at 111

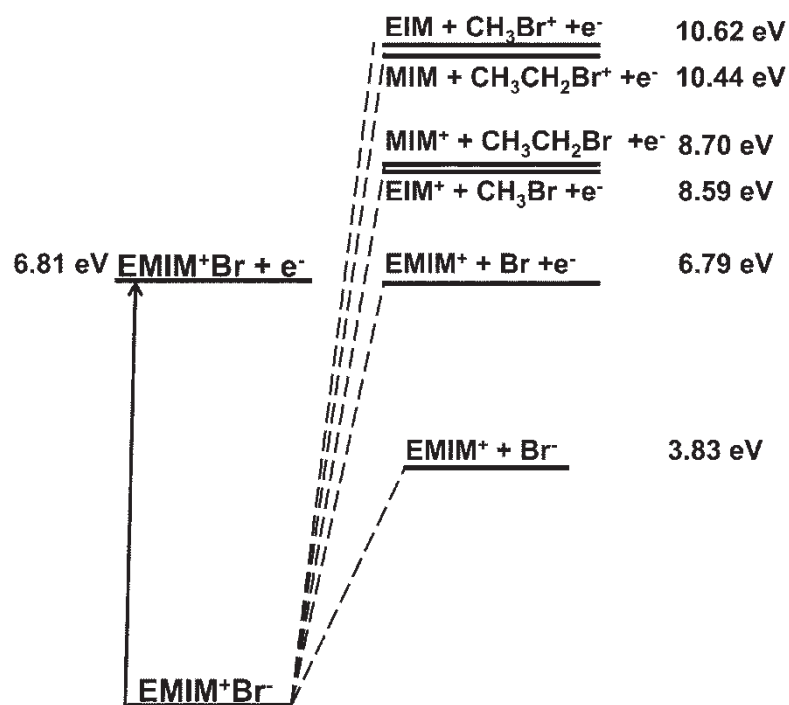
☐ No gas phase IL ion pairs

☐ No dissociative ionization of IL ion pairs

☒ New process for volatilization



Photoionization Energetics of Gas Phase EMIM⁺Br⁻



Is this responsible for 94 & 96 ion masses?

Is this responsible for 108 & 110 ion masses?

Is this responsible for 82 ion mass?

Is this responsible for 96 ion mass?

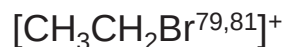
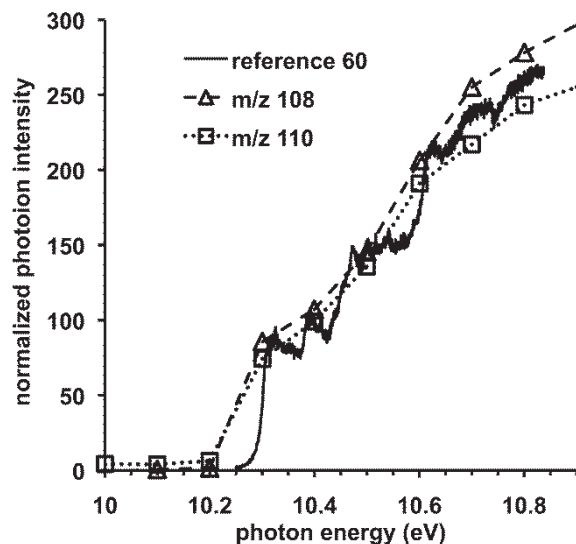
No 111 ion mass

How would you go about detecting this channel?

MP2/6-31+G(d,p), 0 K, ZPVE corrected



Photoionization Efficiency (PIE) Curves

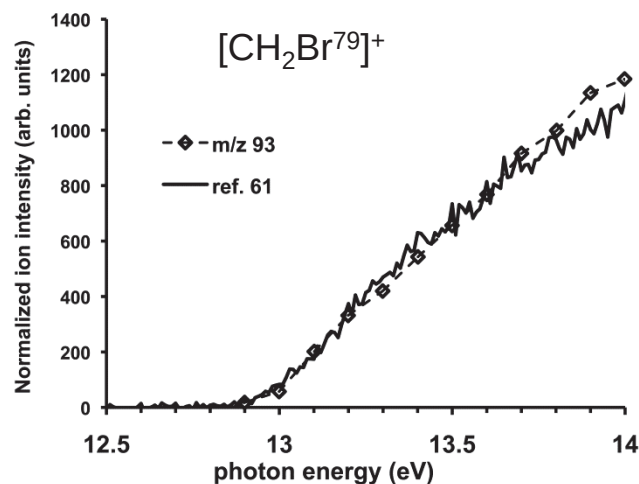
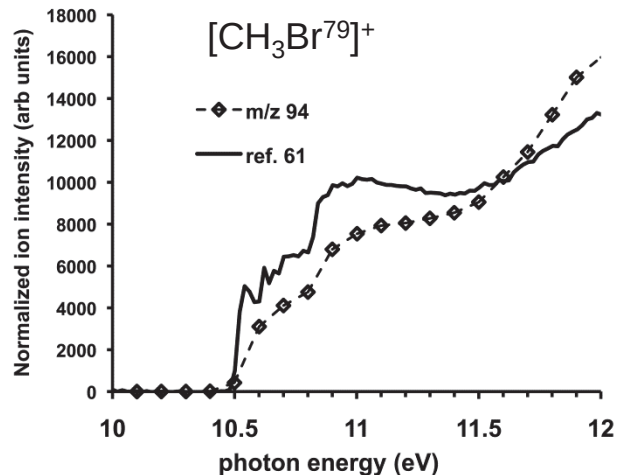


Ref 60:

Baer, T.; Song, Y.; Liu, J.; Chen, W.; Ng, C. Y. *Faraday Discuss.* **2000**, 115, 137

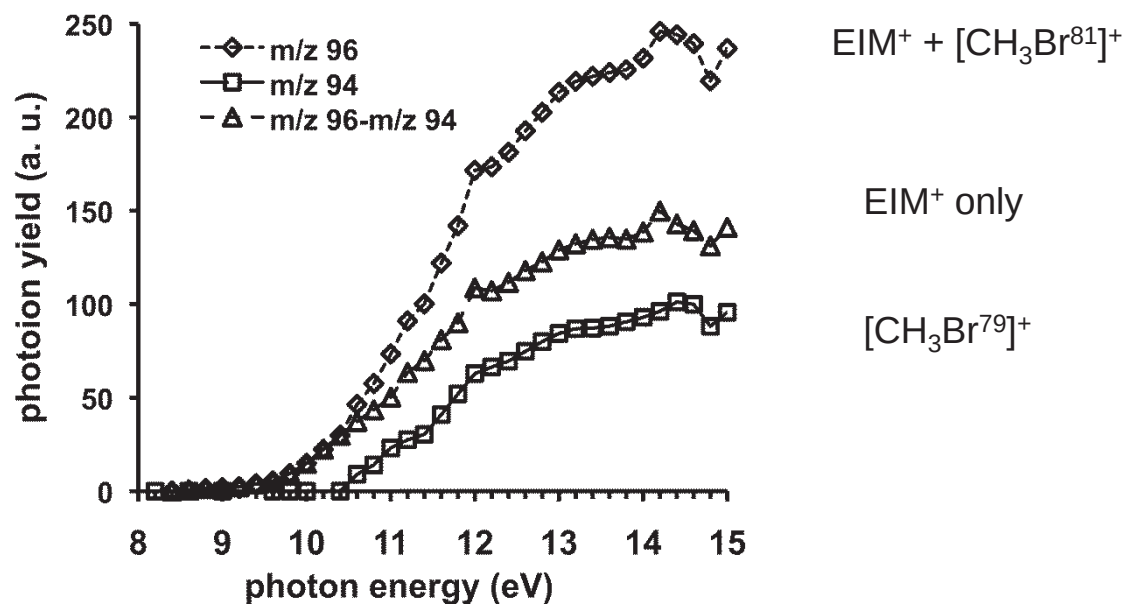
Ref 61:

Locht, R.; Leyh, B.; Dahareng, D.; Hottmann, K.; Jochims, H. W.; Baumgartel, H. *Chem. Phys.* **2006**, 323, 458





Photoionization Efficiency (PIE) Curves

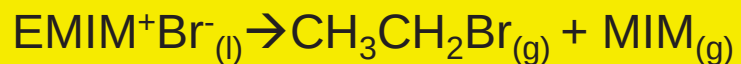


All experimental AEs consistent with MP2 values for dissociative photoionization of IL ion pair but no 111 ion mass

Is there another explanation?

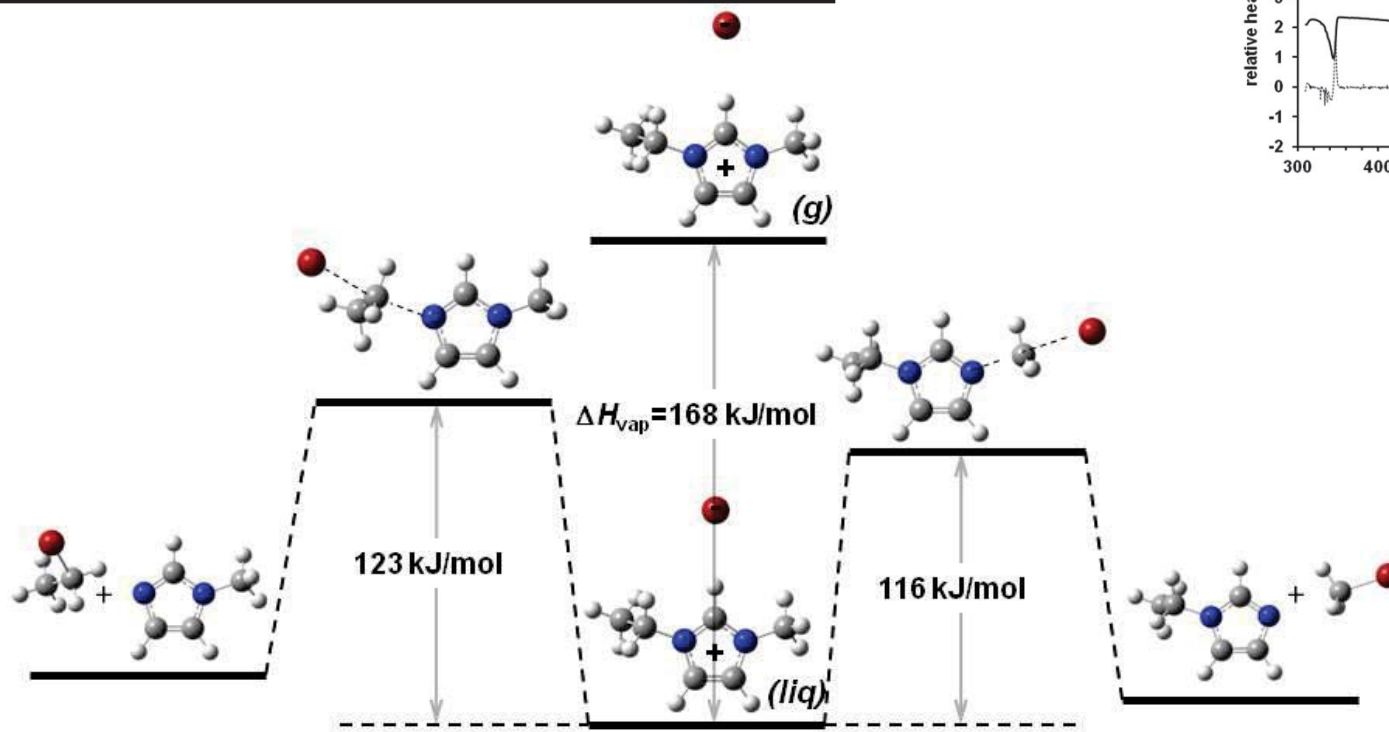
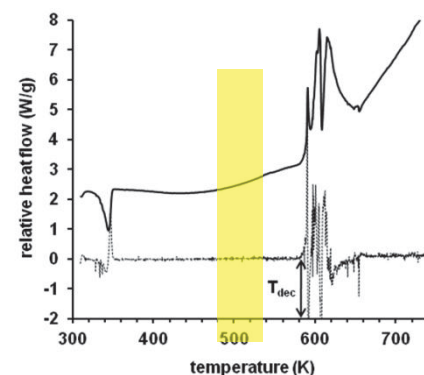


Thermolysis of EMIM⁺Br⁻ can Explain observed PIE curves



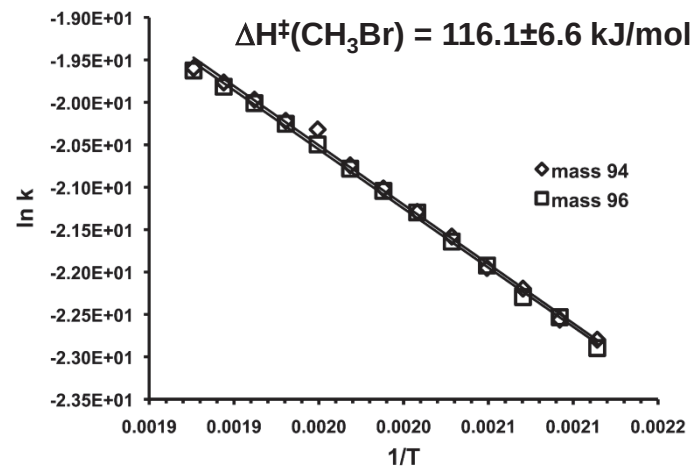
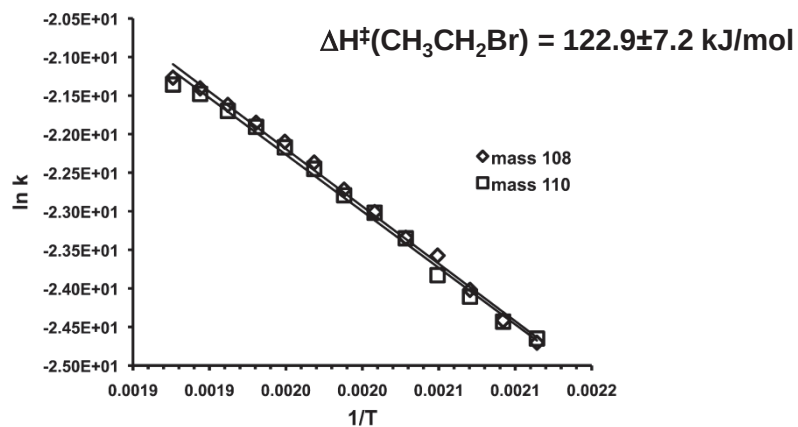
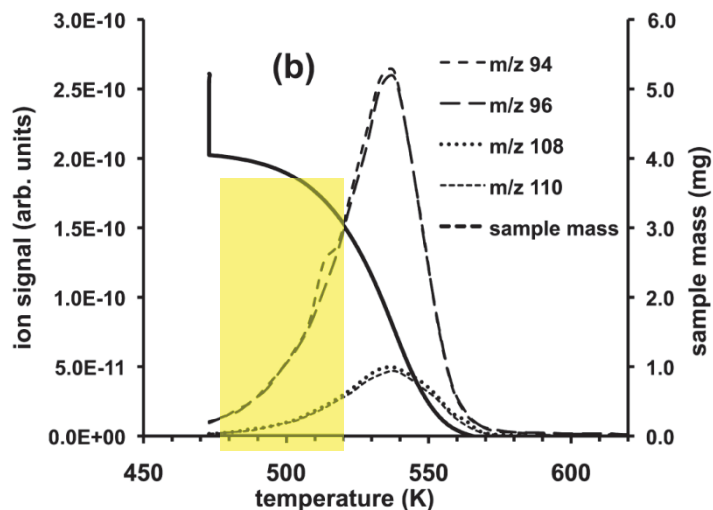
Observed AEs consistent with experimental/MP2/6-31+G(d,p) IEs

VUV beamline is sampling thermolysis not vaporization products





TGA/MS Analysis of EMIM⁺Br⁻ Thermolysis





ΔH_{vap} for EMIM⁺Br⁻ & BMIM⁺Br⁻



MD values

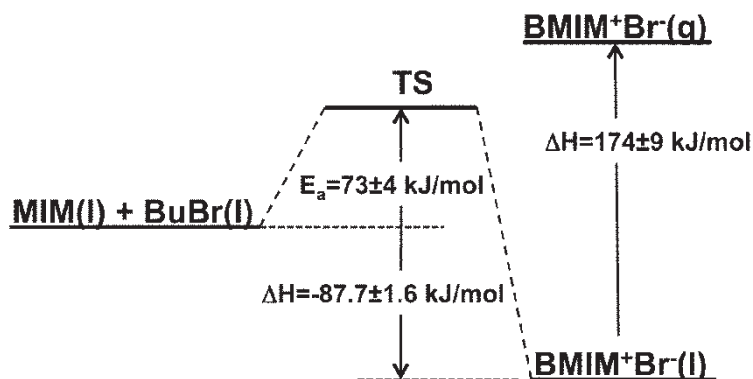
	T (K)	ΔH_{vap} (kJ/mol)
EMIM ⁺ Br ⁻	298	147.1 ^b
EMIM ⁺ Br ⁻	393	138.3 ^a
EMIM ⁺ Br ⁻	473	130.8 ^a
BMIM ⁺ Br ⁻	298	152.8 ^b
BMIM ⁺ Br ⁻	323	150.5 ^a
BMIM ⁺ Br ⁻	393	144.0 ^a

^a MD direct calculation. ^b Linear extrapolation from higher temperature MD values.

298 K values, this study

$$\begin{aligned}\Delta H_{\text{vap}}(\text{EMIM}^+\text{Br}^-) &= 168 \pm 20 \text{ kJ/mol} \\ \Delta H_{\text{f, gas}}(\text{EMIM}^+\text{Br}^-) &= 38.4 \pm 10 \text{ kJ/mol} \\ \Delta H_{\text{f, liq}}(\text{EMIM}^+\text{Br}^-) &= -130 \pm 22 \text{ kJ/mol} \\ \Delta H_{\text{f, gas}}(\text{BMIM}^+\text{Br}^-) &= -5.6 \pm 10 \text{ kJ/mol} \\ \Delta H_{\text{f, liq}}(\text{BMIM}^+\text{Br}^-) &= -180 \pm 20 \text{ kJ/mol}\end{aligned}$$

Calorimetric / *ab initio* values



Paulechka, Y. U.; Kabo, A. G.; Blokhin, A. V. *J. Phys. Chem. B* **2009**, *113*, 14742



Conclusions



- **VUV PI ToF MS spectroscopy has provided**
 - **Structural information on volatilized species from ILs**
 - **AEs & PIE curves, which leads to unique identification**
 - **ΔH_{vap} , which leads to ΔH_{liq} & allows MD calibrations**
 - **Insight into the dynamics of dissociative photoionization**

- **Nature of the IL volatiles are cation/anion dependent**
 - **Ion pairs**
 - **Neutrals from proton transfer**
 - **Neutrals from decomposition**

- **IL combustion is influenced by the nature of the volatiles (fuel)**