Spectroscopy of Gas-Phase Ionic Liquids

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Overview

• Ionic liquids as propellants
• UV spectroscopy of ion pairs
• The next step: IR spectroscopy of ion pairs
• Looking further ahead: A new instrument and spectroscopy of clusters
• Conclusions
Ionic Liquids as Propellants

- Pioneered by Edwards group
- Hypergolic combustion or electric propulsion
- Hydrazine replacement
- Low vapor pressure
- Some vaporize as ion pairs
- Leone: Ionization studies of effusive beam and aerosols
- Viggiano: Gas-phase ion chemistry
- Bemish/Prince: Mass spec studies of ILs in EP
- Calculations from quantum to molecular mechanics
- Spectroscopy limited to liquid; one gas-phase

Wang et al PCCP, 2010, 12, 7246
Ionic Liquids as Propellants

- **Ideal**
  - Test *in silico*
  - Redesign
- **Calculate**
- **Revise theory**
- **Measure**
- **Synthesize**
- **Test in lab**
- **Status Quo**
- **Develop/transition**

**Improve fundamental understanding of ionic liquid physics and chemistry to speed propellant development**
Gas Phase Ion Pairs

- Heating ILs gives ion pairs
- Skimmed supersonic expansion of IL in He
- UV-induced dissociation to cation/anion
- Detect either ion by polarity of TOF

Diagram:
- Time-of-flight mass spectrometer
- Helium
- Glass sample holder (180-240°C)
- UV (210-240 nm)
Gas Phase Ion Pairs

- [emim][Tf2N] is our starter system
- Typical IL tested in EP systems
- High decomposition temp: $T_{\text{onset}} = 455^\circ\text{C}$ [1]
- Vapor pressure: $4 \times 10^{-4}$ torr @201˚C [2]
- Interesting computational question [3]

[N] 
\[ \text{N} \]
\[ \text{O} \]
\[ \text{O} \]
\[ \text{O} \]
\[ \text{N} \]
\[ \text{CF}_3 \]
\[ \text{S} \]

DFT minimum (BE=315 kJ/mol)

MP2 minimum (BE=355 kJ/mol)

[3] Boatz, J, personal communication
When last we met...
UV Spectroscopy of [emim][Tf₂N]

- Detecting [emim] (m/z 111)
- Backing pressure reflects beam temperature
- Spectrum is broad even at low temperature
- Warm spectrum suggests red-absorbing conformers

BE: Boatz, personal communication
IP: Strasser et al, JPCA 111, 3191
UV Photodissociation of [emim][Tf$_2$N]

- 210 nm
- 220 nm
- 225 nm

- Multiphoton
Negative Ion-Detected [emim][Tf$_2$N]

- similar UV absorption to cation
- at least 100x weaker than cation signal

215 nm
Multiple Conformations

• Stacked or planar conformations predicted
• TDDFT suggests different electronic spectra

Stacked
- lower energy conformer (M06 and MP2, not B3LYP)
- first excited state is HOMO-LUMO $\pi-\pi^*$ at 234 nm, f=0.04

Planar
- first four excited states are CT
- second excited state at 220 nm has f=0.01
- fifth excited state is $\pi-\pi^*$ transition at 200 nm, f=0.02

• Better excited state calculations welcome!
IR Calculations

Infrared spectroscopy needed to establish conformers

Calculated intensity

Frequency (cm\(^{-1}\))

MP2
B3LYP
M06
MP2
B3LYP
M06
IR Experiments

**IR spectra using ion depletion**

\[(C^+A^-)^* \rightarrow C^+ + A^-\]

**IR spectra using ion gain**

\[(C^+A^-)^* \rightarrow C^+ + A^-\]
Later this summer...

- Currently limited to ion pairs (and only some of those)
- Electrospray would let us study any ion or charged cluster
- Cold ion trap
- UV photofragmentation
- IR-UV double resonance
- Based on instruments of Rizzo, Johnson, Zwier, etc.
- Could expand to include TOF
Electrospray-Ion Trap Capabilities

UV Spectroscopy of Large Molecules

IR Spectroscopy of Large Molecules

Electrospray-Ion Trap Capabilities

UV and IR Spectroscopy of Clusters

Nagornova, Rizzo, and Boyarkin, Science, 336, 320 (2012)
Outlook

• IR spectroscopy of [emim][Tf$_2$N], other ion pairs (this summer)
• Bring new machine online (late summer/fall)
• UV and IR spectroscopy of [emim], [bmpy], [dca], [Tf$_2$N] clusters (2013)
• Fuel/oxidizer reaction chemistry in ion trap (2013)
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