

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE (DD-MM-YYYY) July 2014		2. REPORT TYPE Briefing Charts		3. DATES COVERED (From - To) July 2014- August 2014	
4. TITLE AND SUBTITLE Recent Advances in Understanding the Reactivity of Energetic Ionic Liquids in Propulsion Applications				5a. CONTRACT NUMBER FA9300-06-C-0023	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Steven D. Chambreau				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER QORA	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQRP 10 E. Saturn Blvd. Edwards AFB CA 93524-7680				8. PERFORMING ORGANIZATION REPORT NO.	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQR 5 Pollux Drive. Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-RQ-ED-VG-2014-238	
12. DISTRIBUTION / AVAILABILITY STATEMENT Distribution A: Approved for Public Release; Distribution Unlimited.					
13. SUPPLEMENTARY NOTES Briefing Charts presented at ACS, San Francisco, CA, 10-14 Aug, 2014. PA#14406					
14. ABSTRACT The interest in using energetic ionic liquids (EILs) to replace highly toxic and volatile hydrazine-based fuels stems from the inherently low vapor pressure of ionic liquids. Understanding the reactivity of EILs in propulsion applications has included both experimental and theoretical investigations, but is complicated by the fast and complex chemistry involved during ignition and combustion of the propellants. Recently, the availability of a polarizable continuum model variant called the generic ionic liquid (GIL) model, developed by Truhlar and co-workers, has enabled the investigation of anion properties such as basicity and nucleophilicity in the condensed phase. Both the basicity and nucleophilicity of the anion influence the thermal decomposition of ionic liquids and understanding basicity of the anion is important in interpreting hypergolic ignition mechanisms in dicyanamide-based EILs. An approach using the GIL has been developed to understand both basicity and nucleophilicity trends in EILs, the results of which are presented in this paper. Also, recent experimental investigations using reactive surface scattering techniques and tunable vacuum ultraviolet photoionization of catalytically decomposed aerosols of EILs will be discussed.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 30	19a. NAME OF RESPONSIBLE PERSON Steve Schneider
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NO (include area code) 661-275-5759

Standard Form
298 (Rev. 8-98)
Prescribed by ANSI
Std. Z39.18



AFRL
THE AIR FORCE RESEARCH LABORATORY
LEAD | DISCOVER | DEVELOP | DELIVER



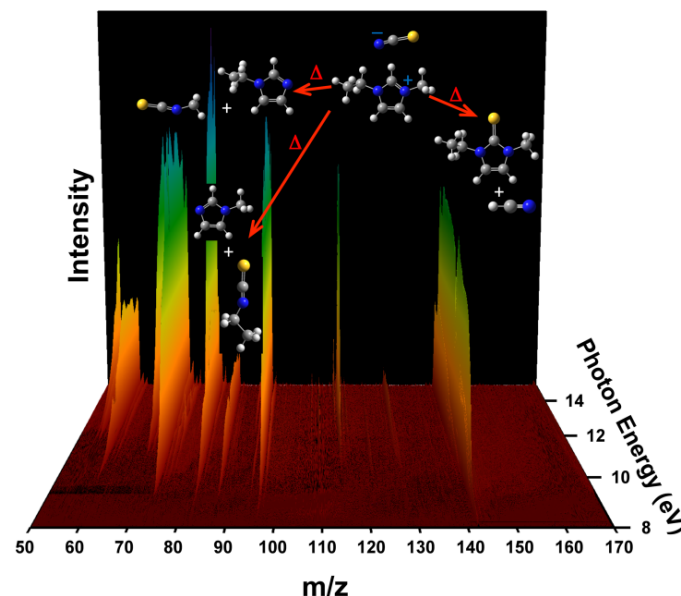
Recent advances in understanding the reactivity of energetic ionic liquids in propulsion applications

Steven D. Chambreau

*American Chemical Society Fall 2014 National Conference
August 12, 2014*

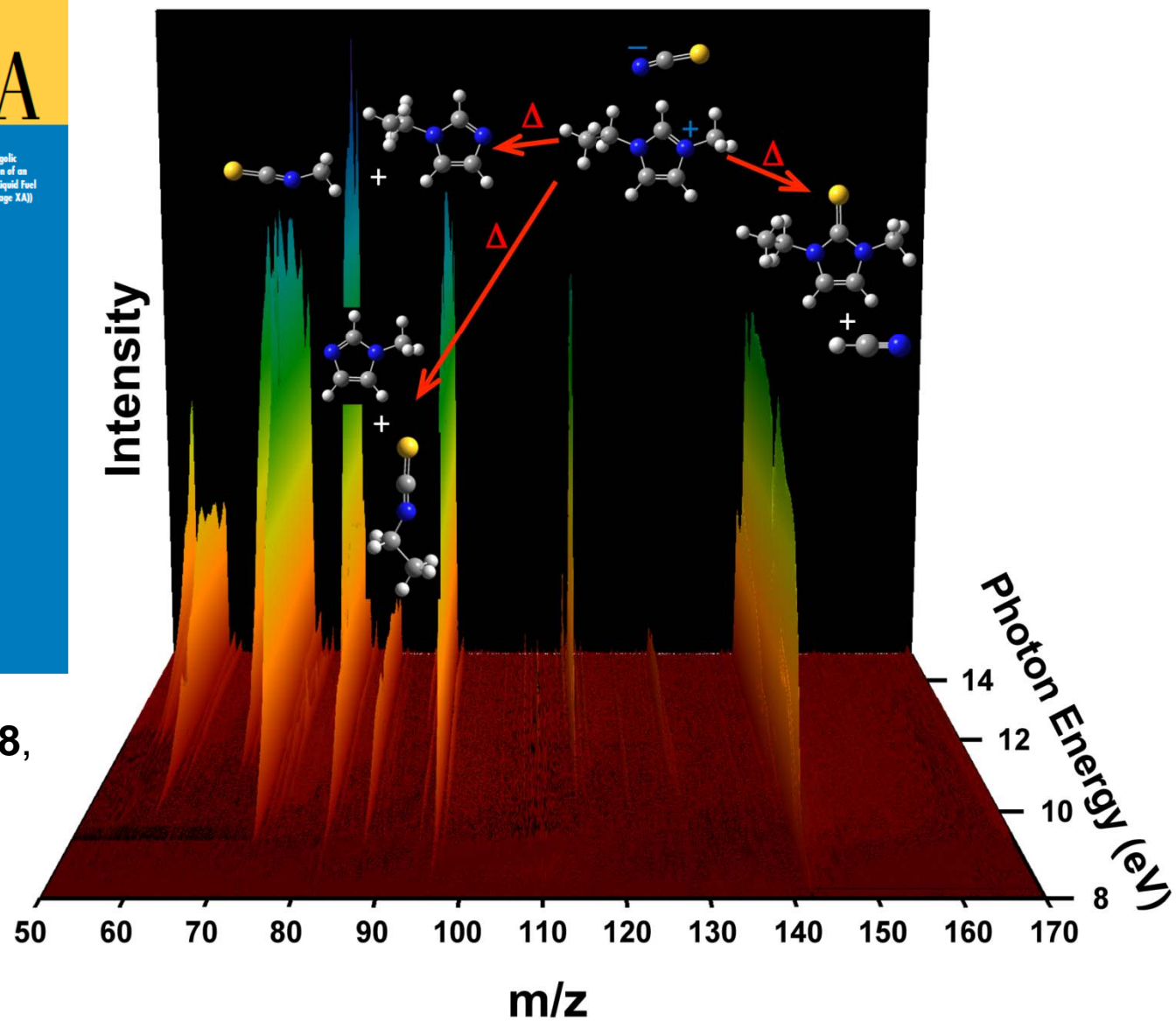
*ERC, Inc.
Propellants Branch
Space and Missile Propulsion Division
Air Force Research Laboratory
AFRL/RQRP
10 E Saturn Blvd
Edwards AFB, CA 93524*

*Tel: 661 275 6176
Fax: 661 275 5471
Email: steven.chambreau.ctr@us.af.mil*





J. Phys. Chem. A, 2008,
112, 7816-7824.



J. Am. Chem. Soc., submitted 2014



Outline



- Introduction
- Thermal decomposition of ionic liquids
 - Basicity & nucleophilicity
 - gas phase vs. GIL model
- Reactive scattering
- VUV-PIMS of catalytic ionic liquid reactivity



Motivation

- Replacement for monomethylhydrazine + N_2O_4
(highly volatile and toxic!!)



Distribution A: Approved for public release; distribution unlimited



GIL model



THE JOURNAL OF
PHYSICAL CHEMISTRY B

Article

pubs.acs.org/JPCB

Quantum Mechanical Continuum Solvation Models for Ionic Liquids

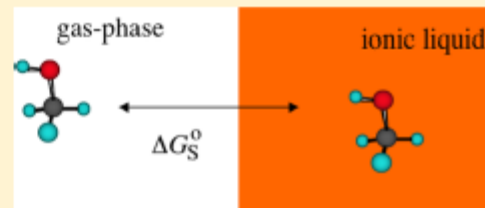
Varinia S. Bernales,[†] Aleksandr V. Marenich,[‡] Renato Contreras,^{*,†} Christopher J. Cramer,^{*,‡}
and Donald G. Truhlar^{*,‡}

[†]Departamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile

[‡]Department of Chemistry and Supercomputing Institute, University of Minnesota, 207 Pleasant Street SE, Minneapolis, Minnesota 55455, United States

S Supporting Information

ABSTRACT: The quantum mechanical SMD continuum universal solvation model can be applied to predict the free energy of solvation of any solute in any solvent following specification of various macroscopic solvent parameters. For three ionic liquids where these descriptors are readily available, the SMD solvation model exhibits a mean unsigned error of 0.48 kcal/mol for 93 solvation free energies of neutral solutes and a mean unsigned error of 1.10 kcal/mol for 148 water-to-IL transfer free energies. Because the necessary solvent parameters are *not* always available for a given ionic liquid, we determine average values for a set of ionic liquids over which measurements *have* been made in order to define a generic ionic liquid solvation model, SMD-GIL. Considering 11 different ionic liquids, the SMD-GIL solvation model exhibits a mean unsigned error of 0.43 kcal/mol for 344 solvation free energies of neutral solutes and a mean unsigned error of 0.61 kcal/mol for 431 water-to-IL transfer free energies. As these errors are similar in magnitude to those typically observed when applying continuum solvation models to ordinary liquids, we conclude that the SMD universal solvation model may be applied to ionic liquids as well as ordinary liquids.



J. Phys. Chem. B **2012**, 116, 9122–9129

Distribution A: Approved for public release; distribution unlimited



GIL model



- How do we predict basicity and nucleophilicity in any ionic liquid?
- GIL model is polarizable continuum model benchmarked to treat ionic liquids in general.



Basicity: ΔG_{acid}

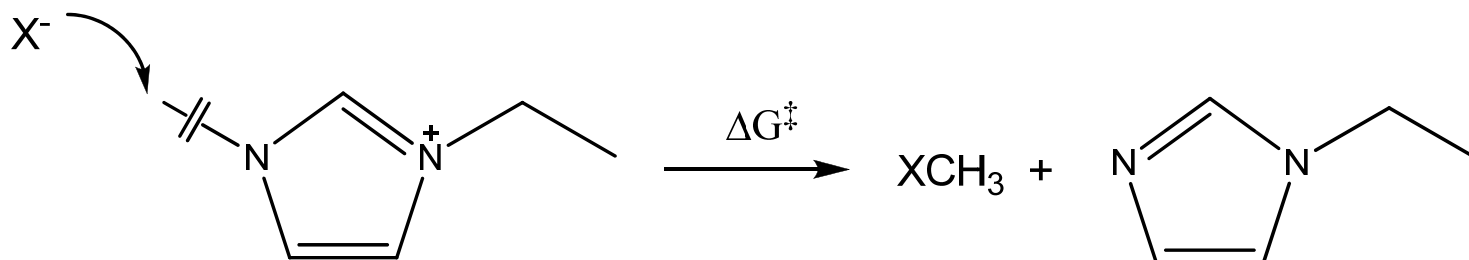


	$\Delta G_{\text{acid}}(\text{g})$ (kJ/mol)		$\Delta G_{\text{acid}}(\text{l})$ SMD-GIL (kJ/mol)		$\Delta G_{\text{acid}}(\text{l})$ SMD-H ₂ O (kJ/mol)
HNCS	1332.5	HNCS	607.0	HNCS	549.5
HNO ₃	1306.7	HNCNCN	578.0	HNCNCN	521.8
HSCN	1274.2	HNO ₃	566.6	NCNHCN	495.9
HNCNCN	1272.6	NCNHCN	550.3	HNO ₃	494.9
NCNHCN	1234.6	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

basicity: $\text{SCN}^- > \text{N}(\text{CN})_2^- > \text{NO}_3^- > \text{TCM}^-$



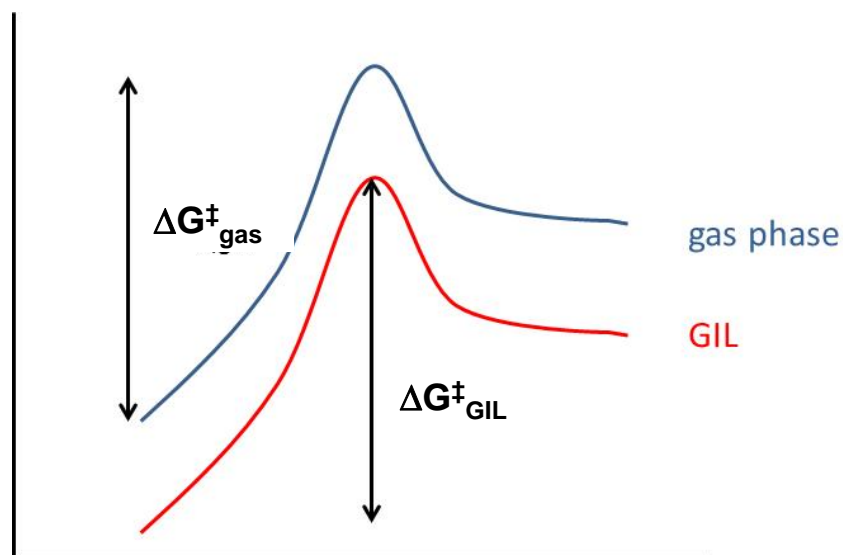
Anion Nucleophilicity



X = Br, SCN, dca, TCM

The energy differences between the gas phase and GIL condensed phase species is approximately constant:
($E_{a,gas} \sim E_{a,GIL}$)

IL	method	ΔG^\ddagger (kJ/mol)	ΔG (gas-->liquid) (kJ/mol)
EMIM ⁺ Br ⁻	M06	138.6	-6.5
	GIL	134.6	-4.0
EMIM ⁺ dca ⁻	M06	163.6	-1.7
	GIL	158.2	-5.4
EMIM ⁺ SCN ⁻	M06	151.2	-2.2
	GIL	153.4	2.2
EMIM ⁺ TCM ⁻	M06	175.8	-0.8
	GIL	181.5	5.7



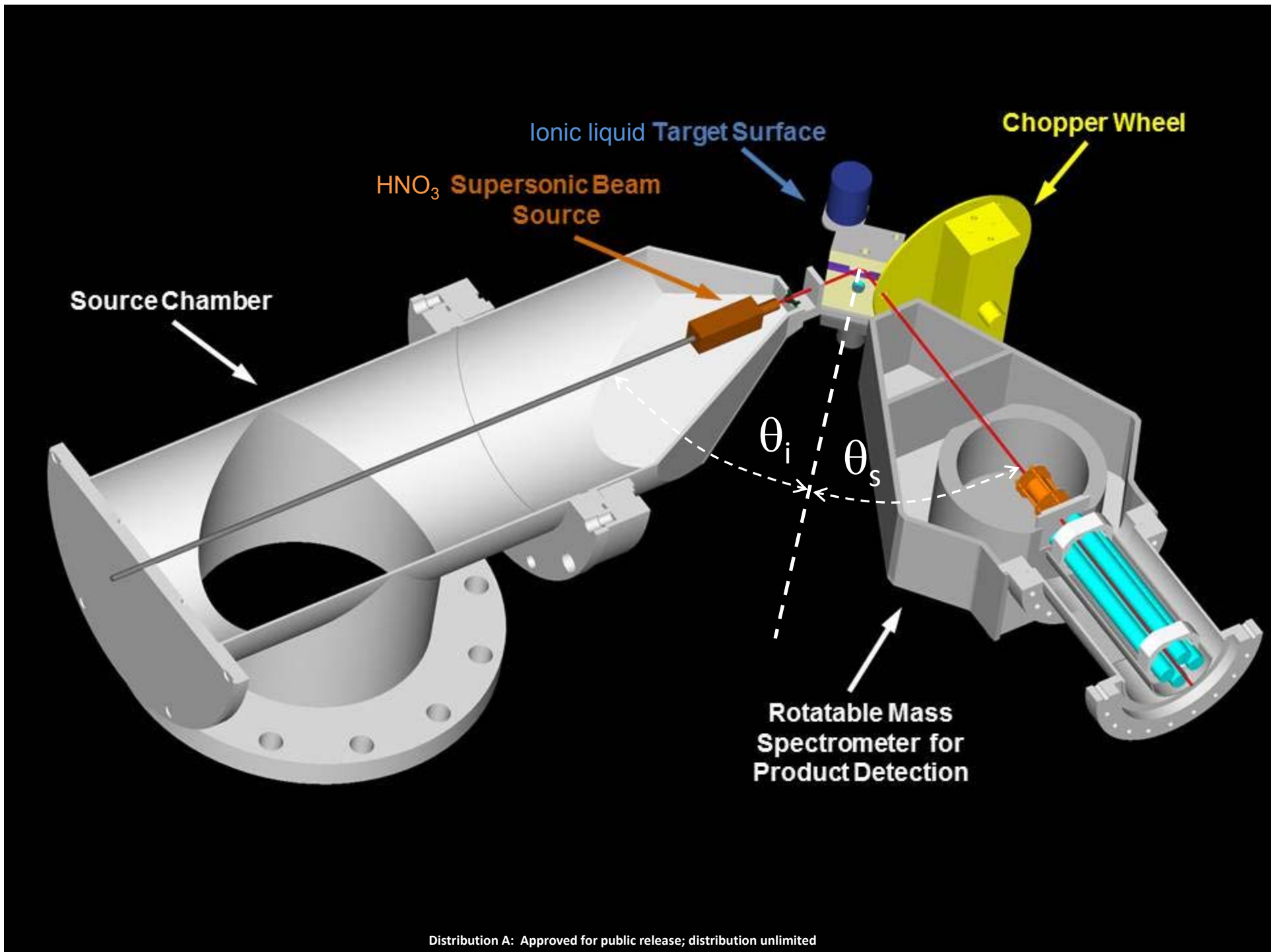
Nucleophilicity: Br⁻ > SCN⁻ > dca⁻ > TCM⁻

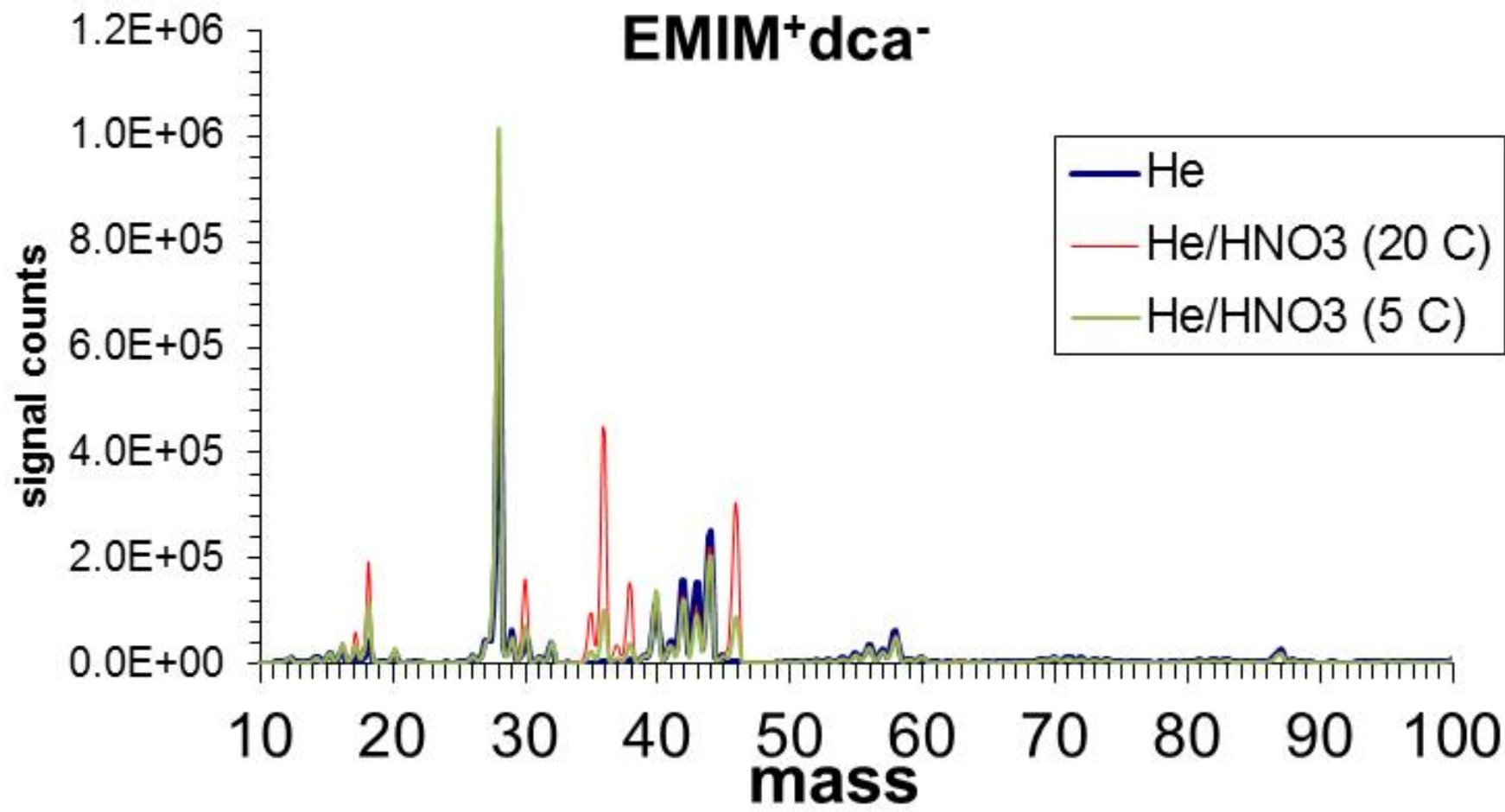


Reactive scattering of HNO_3 off of $\text{EMIM}^+\text{dca}^-$



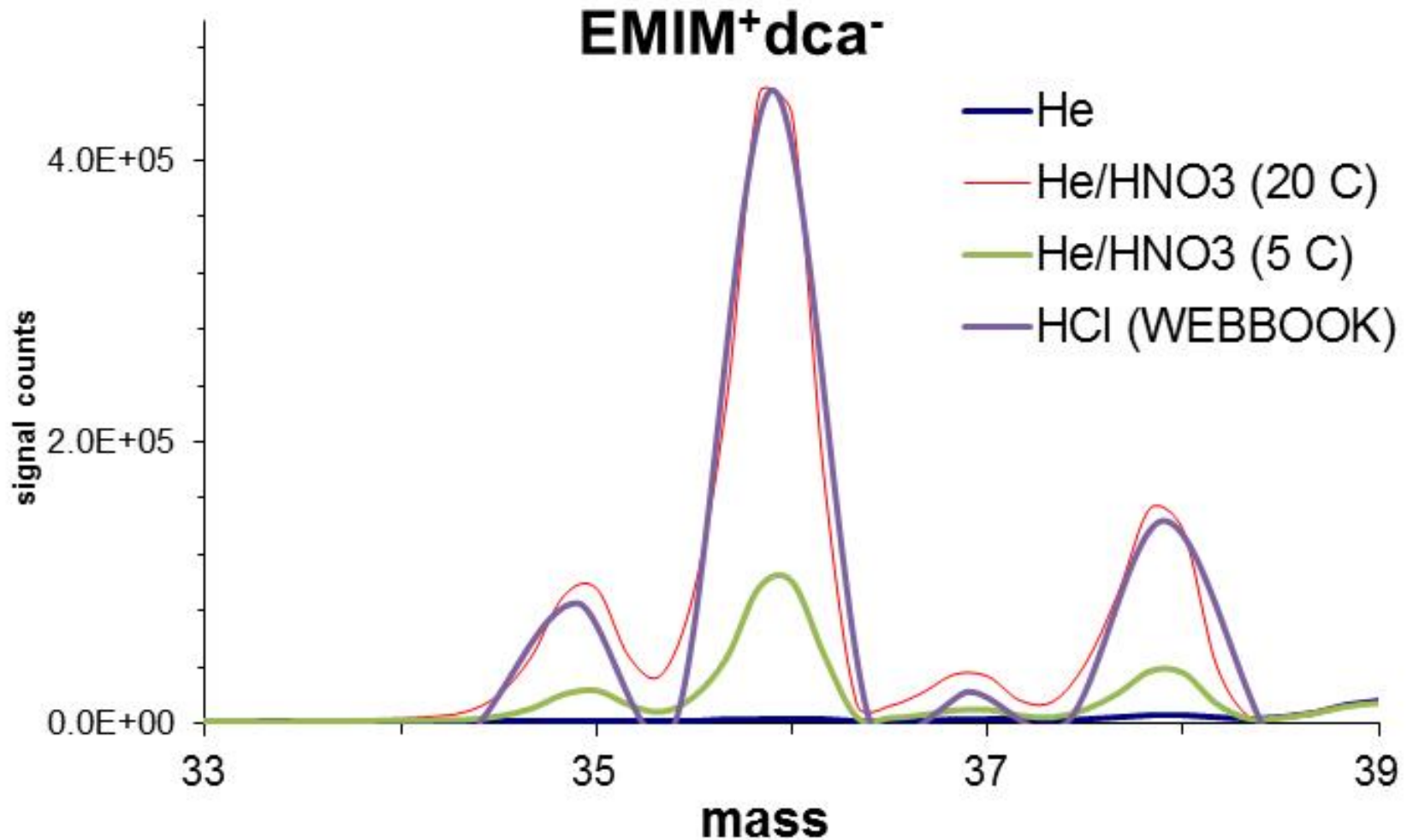
- Can we detect protonated dca^- ?







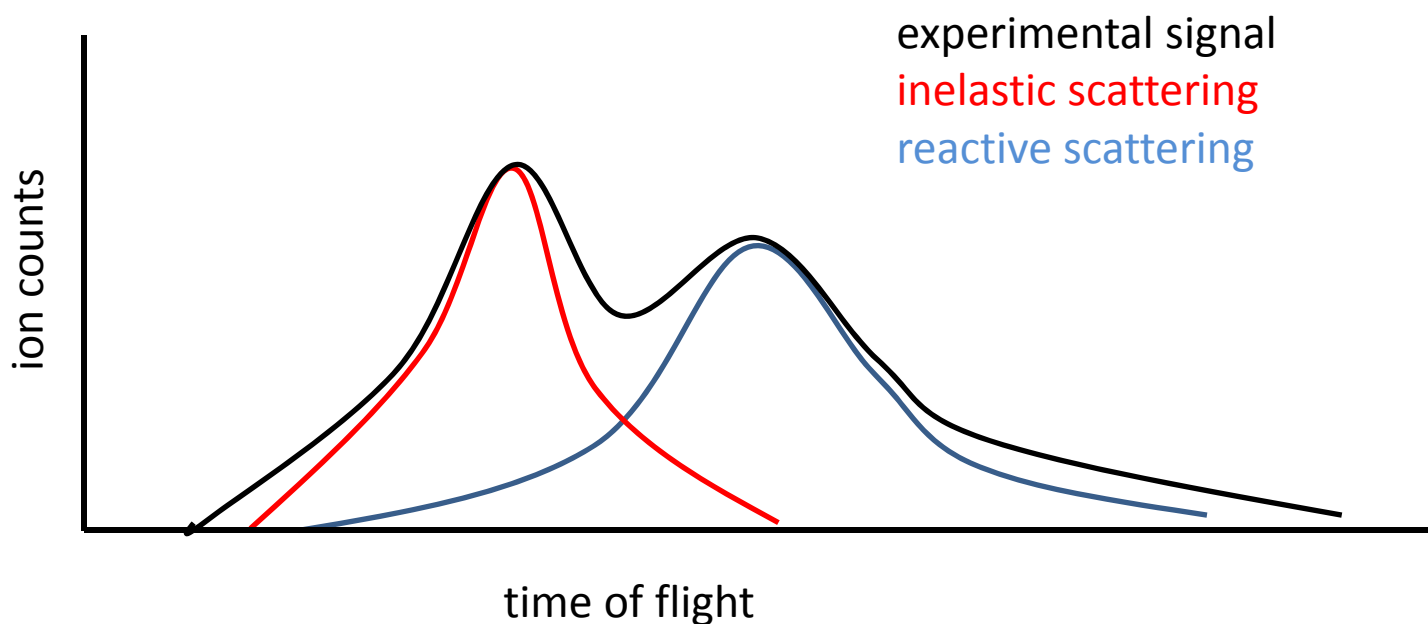
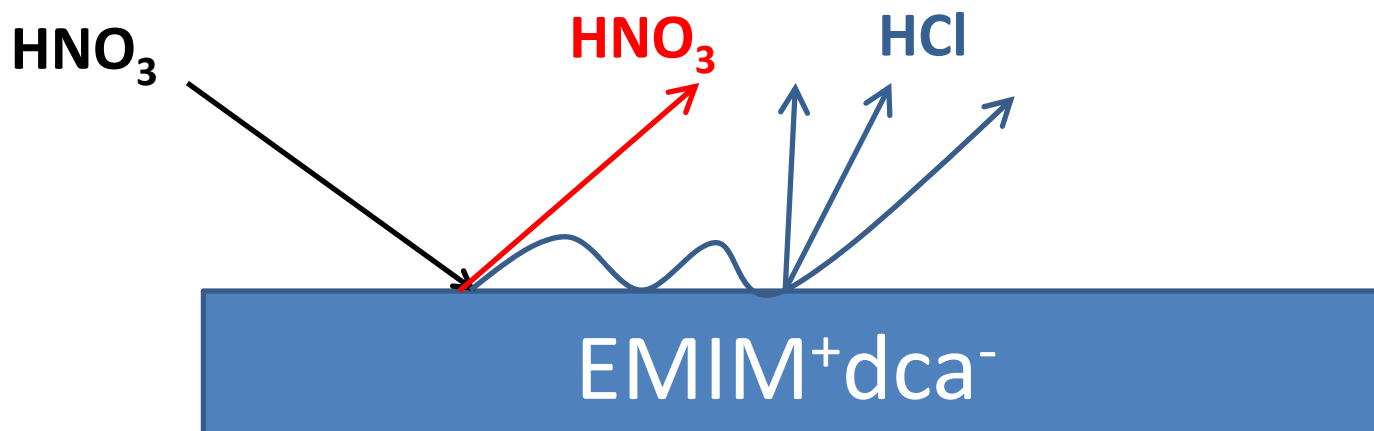
Comparison with reference HCl mass spectrum



Masses 35-38 are likely $^{35}\text{Cl}^+$, H^{35}Cl^+ , $^{36}\text{Cl}^+$ and H^{37}Cl^+



scattering processes





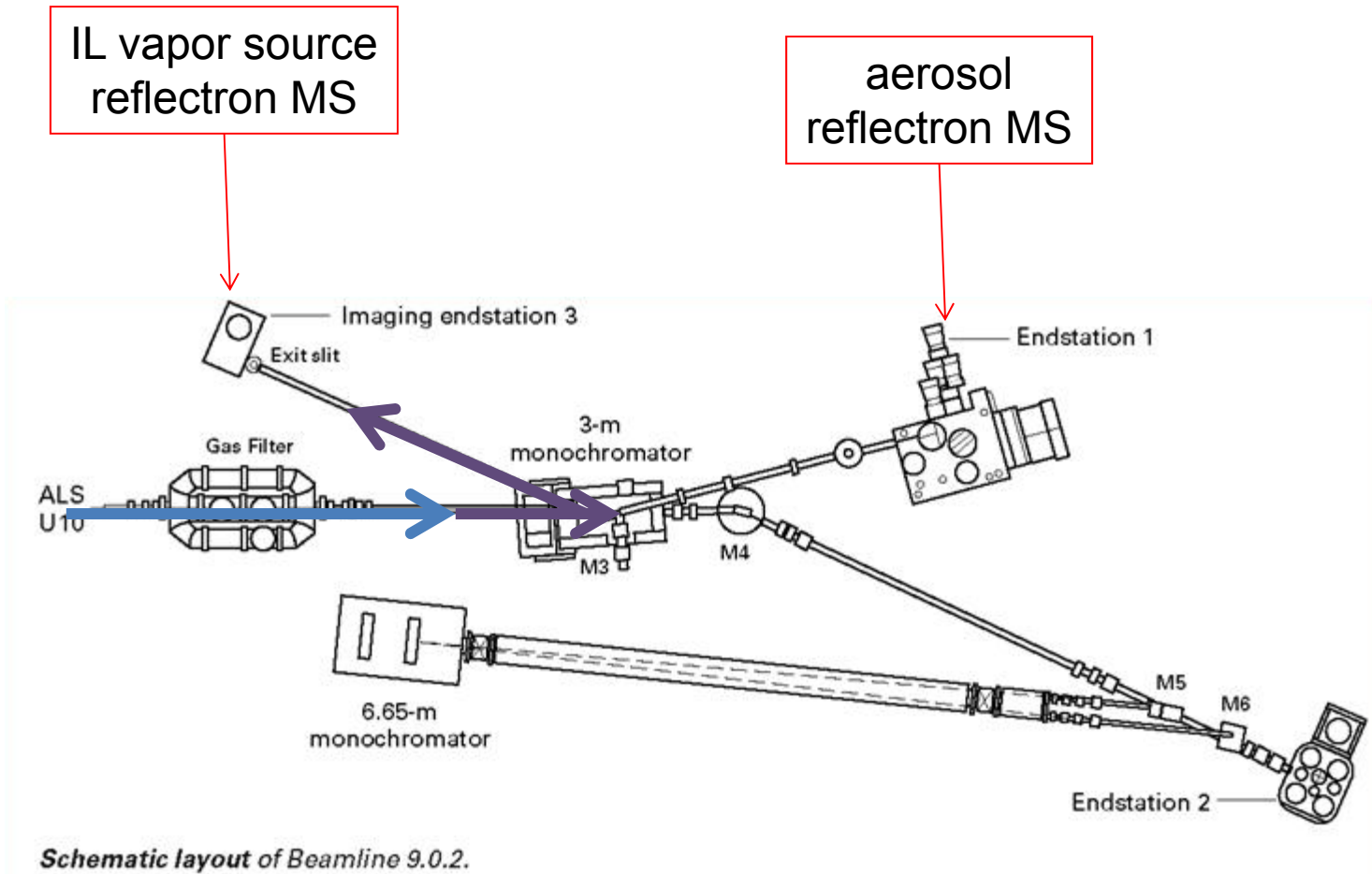
Synthesis of dca⁻ ILs



- cation chloride salt prepared.
- Ag⁺dca⁻ added and Ag⁺Cl⁻ precipitates out.
 - 1000 ppm Cl⁻ remains as an impurity.
- Halide-free synthesis?



ALS: Chemical Dynamics Beamline



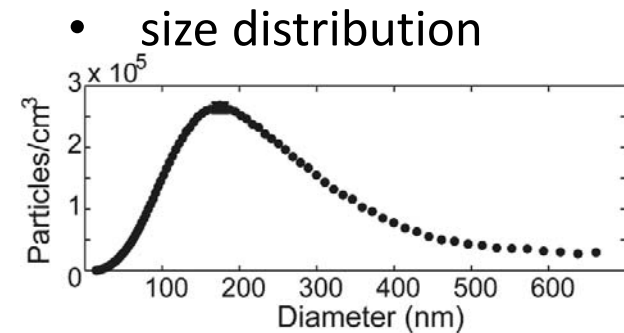
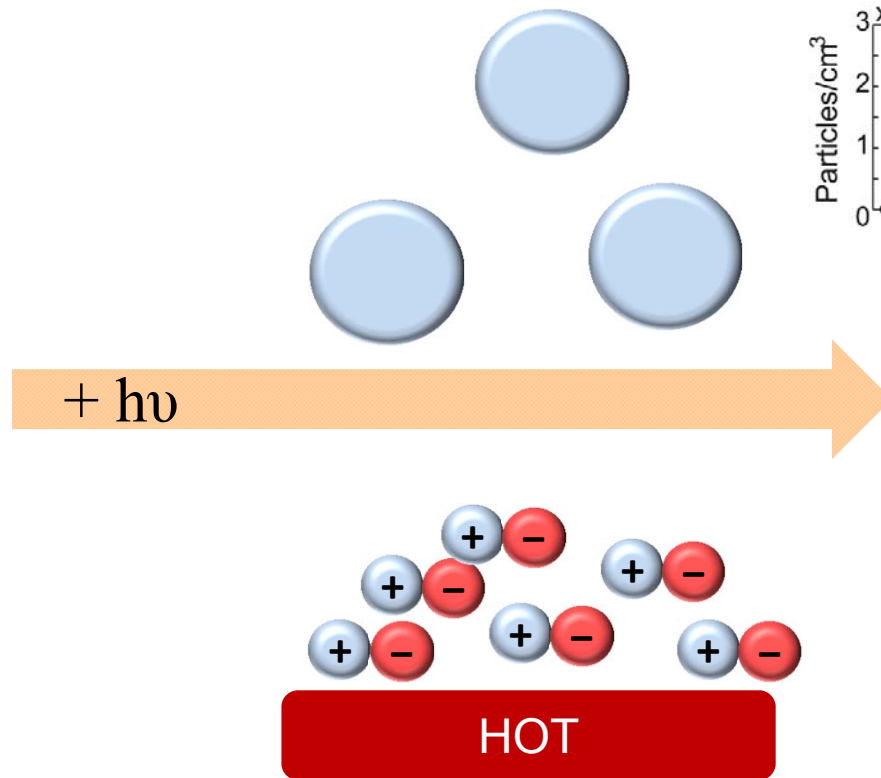
7.4-15.0 eV photons, 0.025 eV resolution



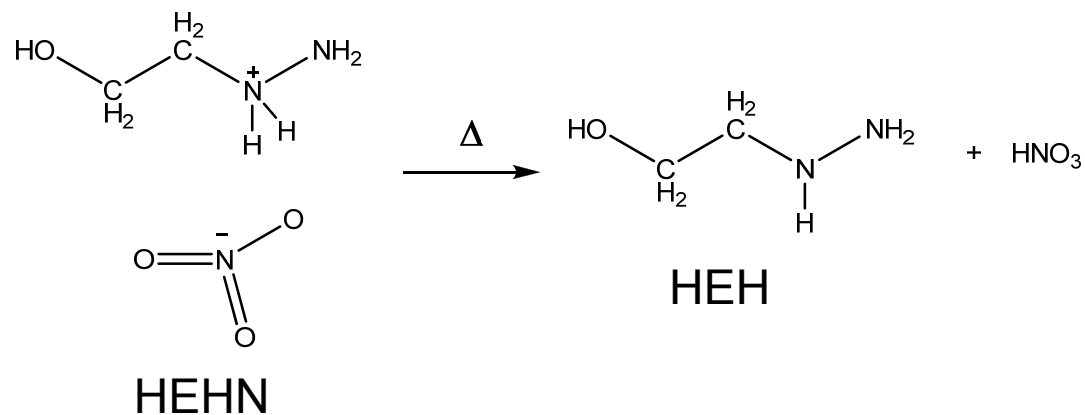
IL Aerosol reactivity



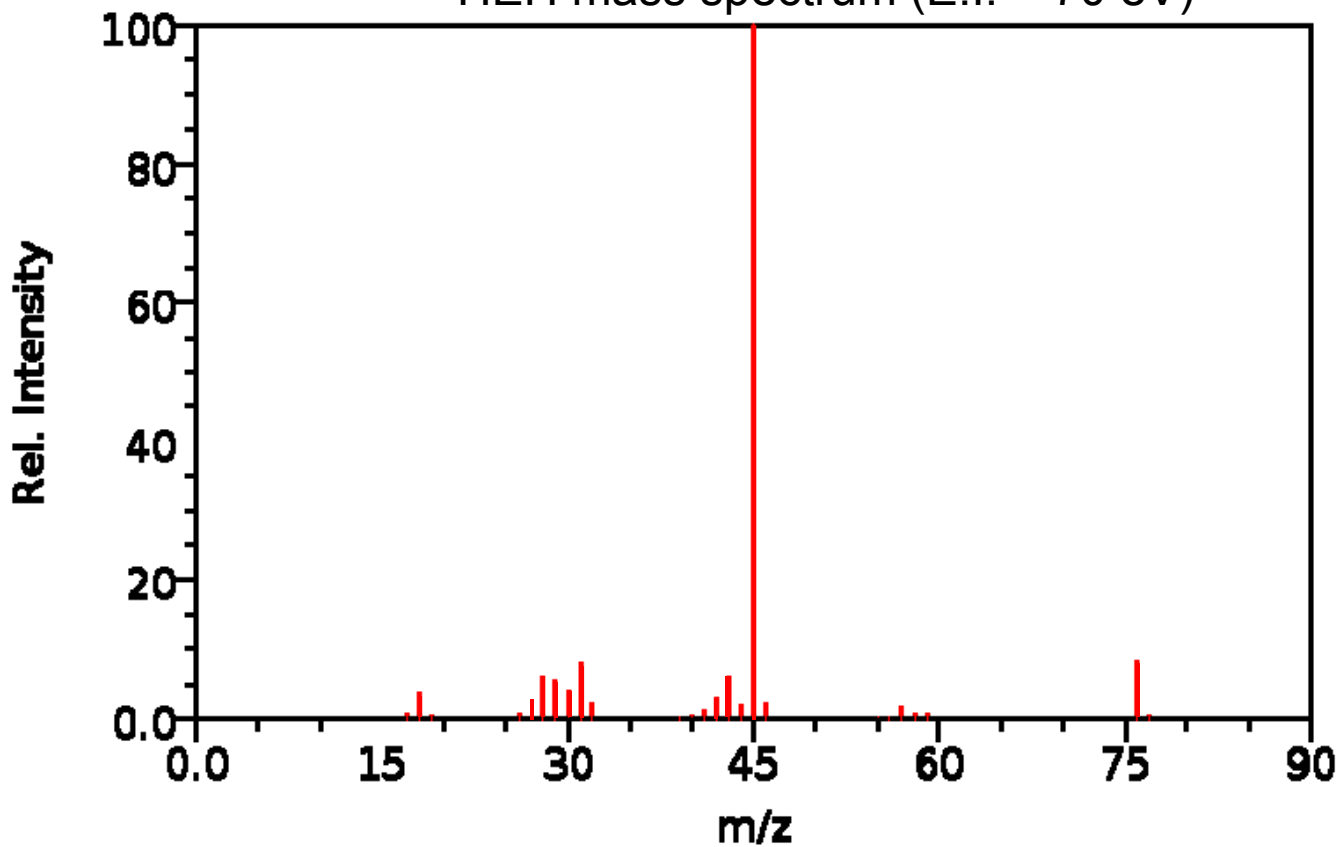
- ILs have very low vapor pressures:
 - Aerosols are liquid droplets suspended in gas phase:



Reaction dynamics
and kinetics

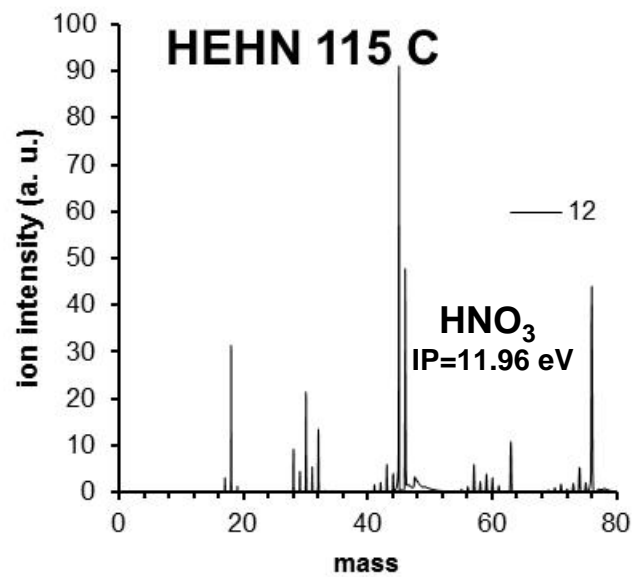
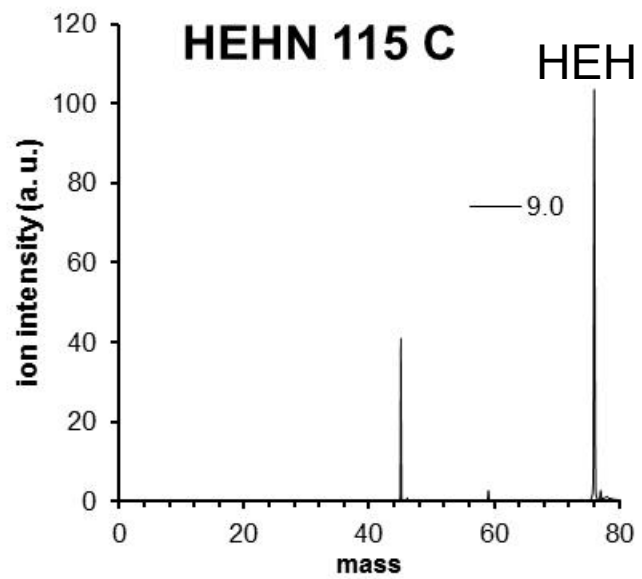


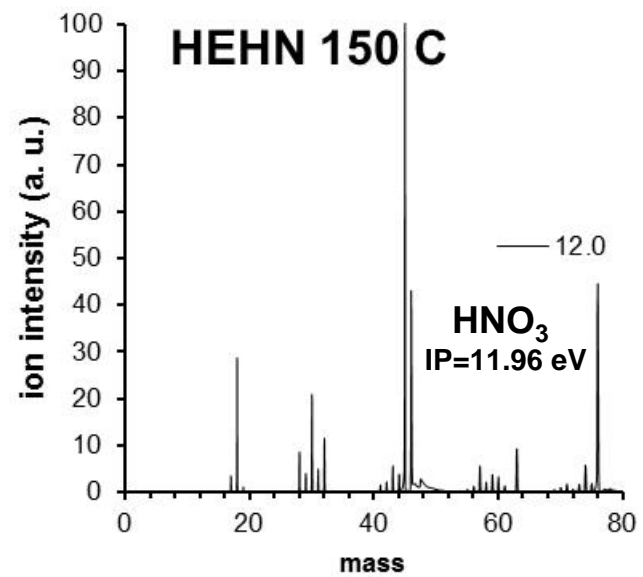
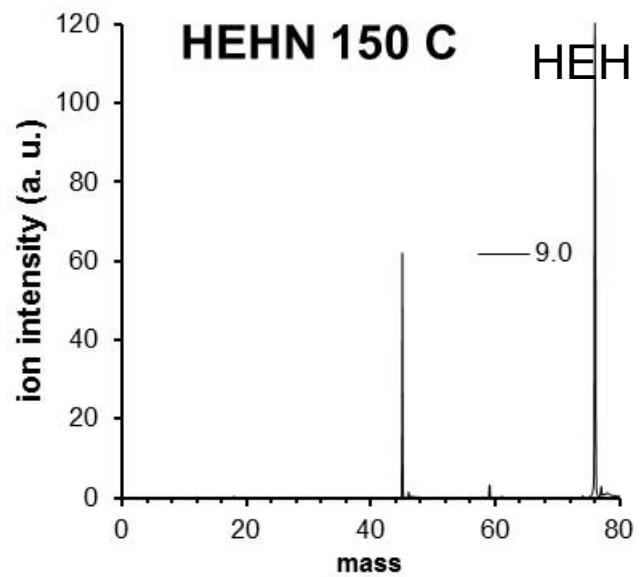
HEH mass spectrum (E.I. ~ 70 eV)

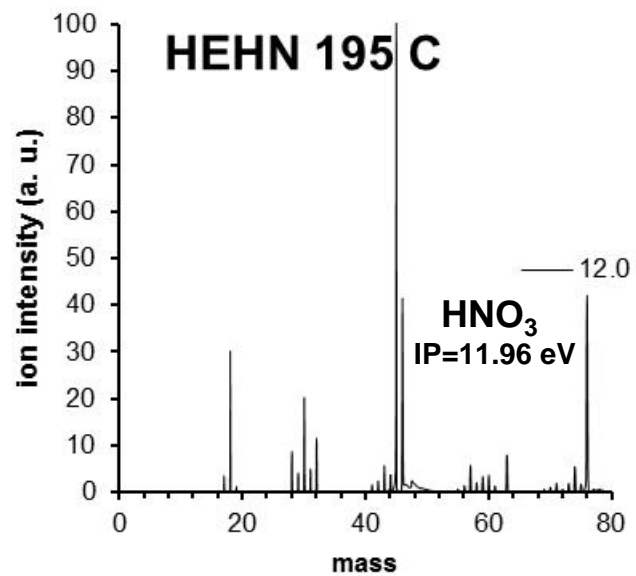
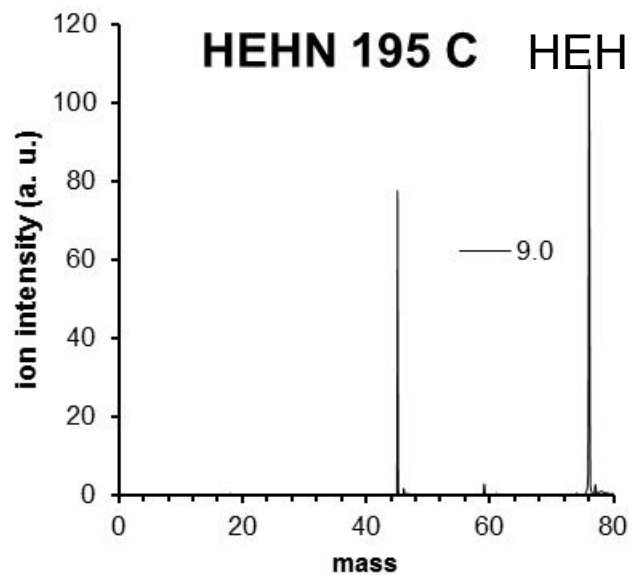


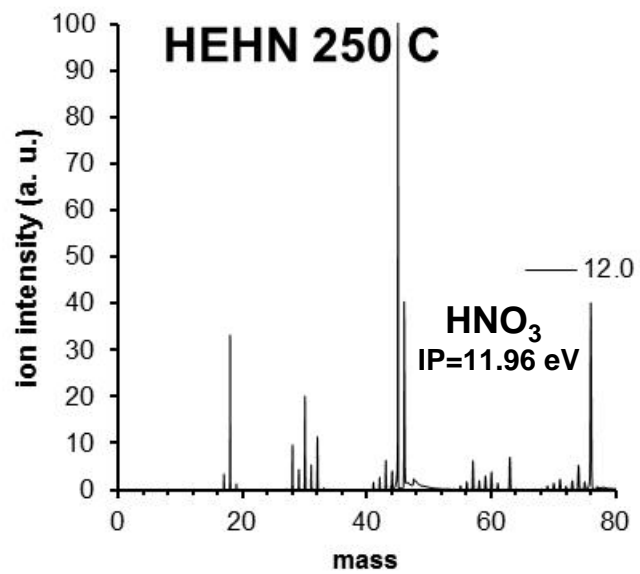
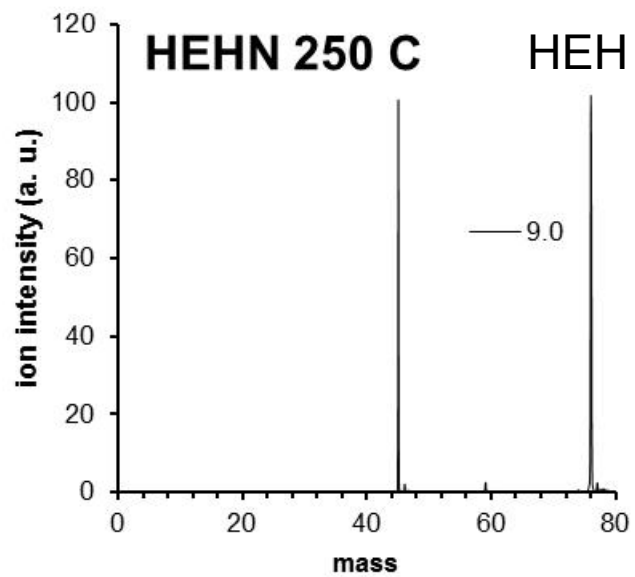
NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

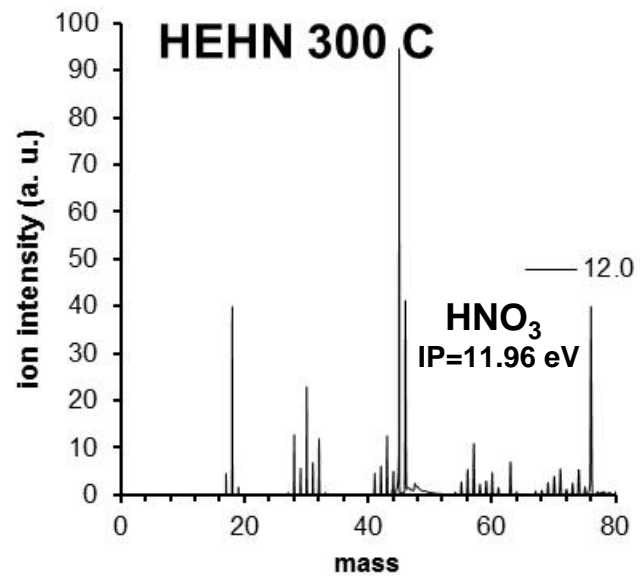
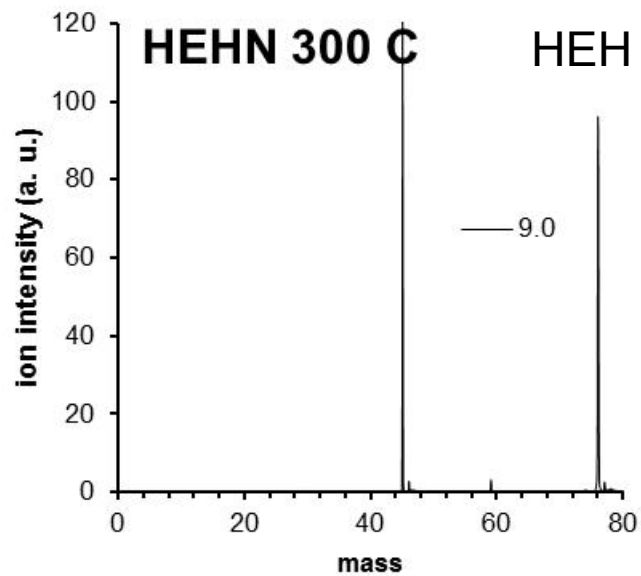
Distribution A: Approved for public release; distribution unlimited



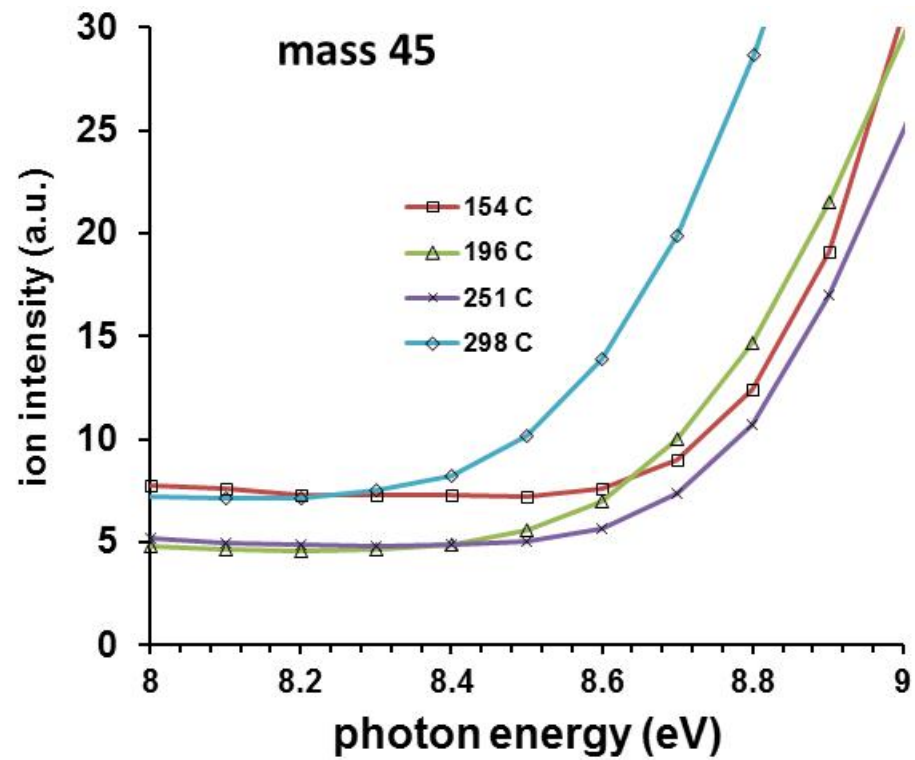
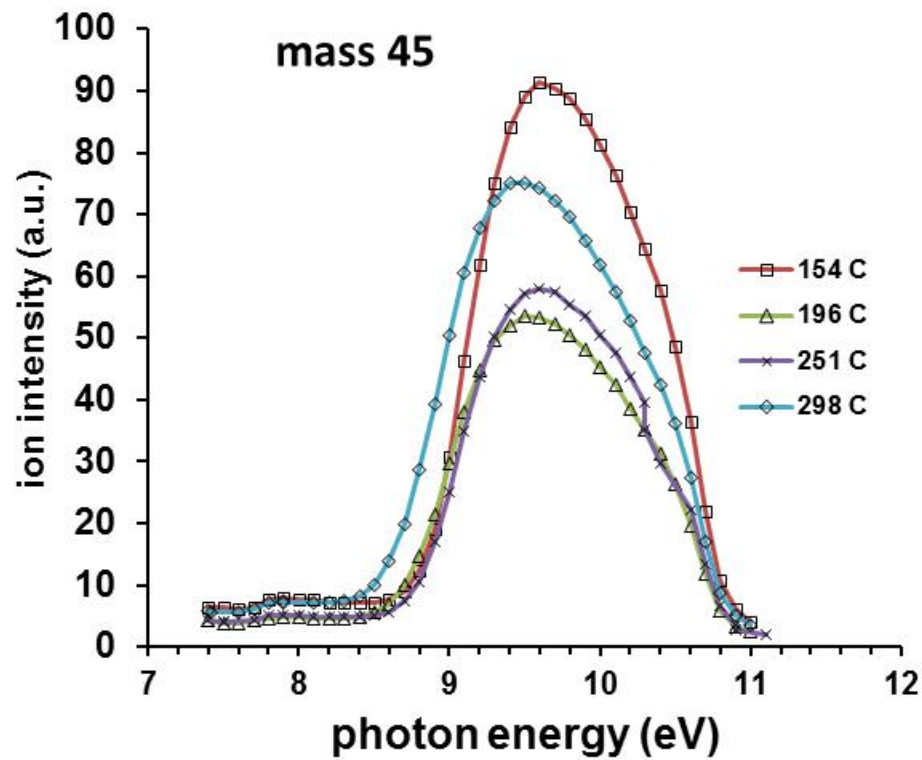




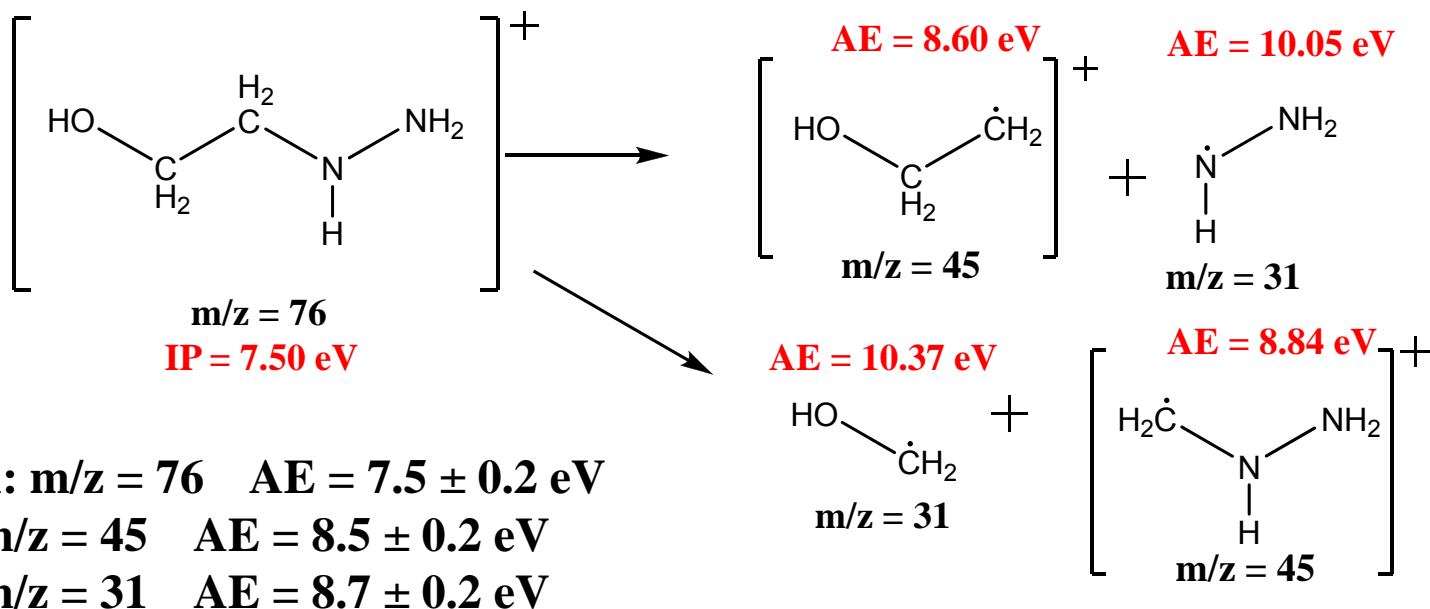




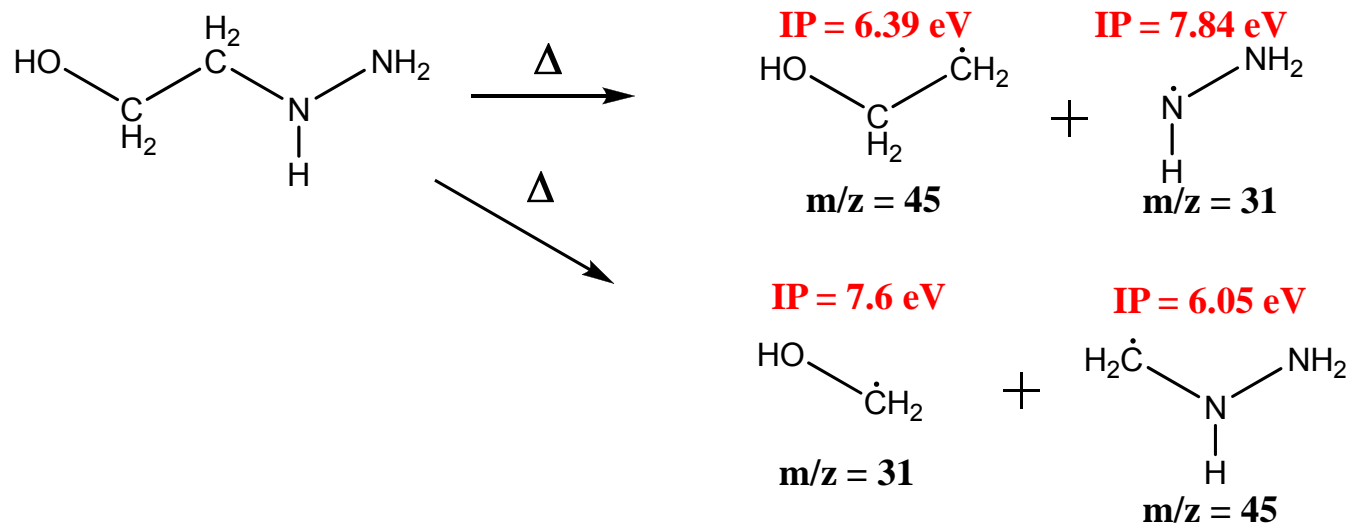
no HEH thermal decomposition products!



photoionization,
fragmentation:

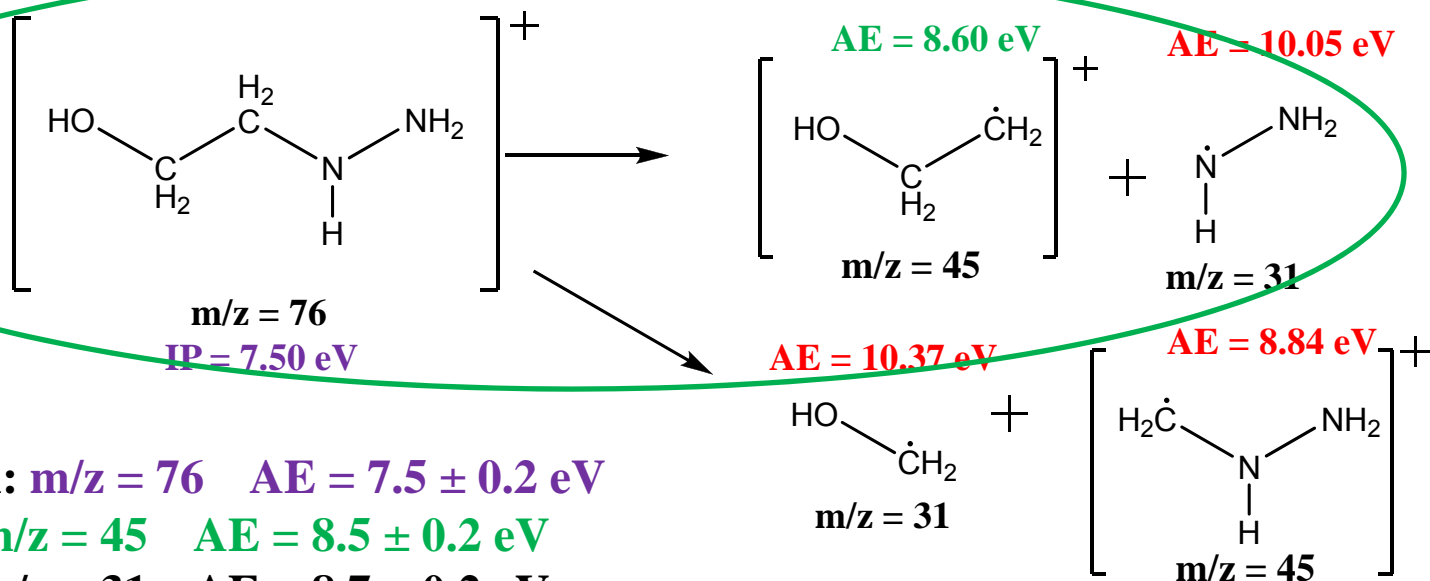


thermal
decomposition,
photoionization:



M06/6-31+G(d,p)

photoionization,
fragmentation:

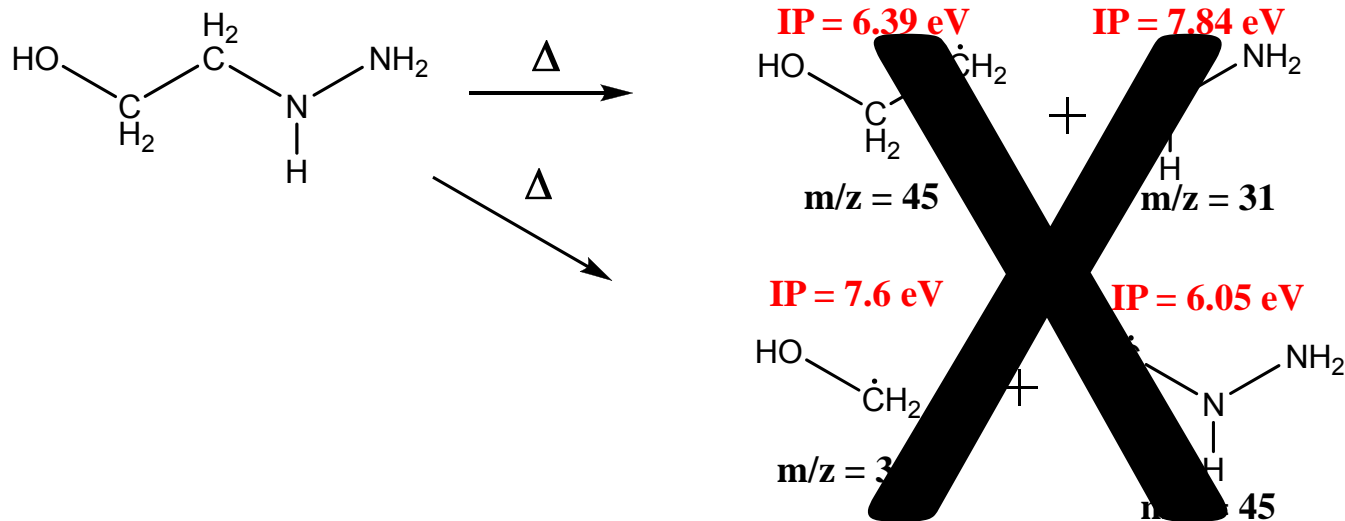


Experimental: $m/z = 76$ $AE = 7.5 \pm 0.2 \text{ eV}$

$m/z = 45$ $AE = 8.5 \pm 0.2 \text{ eV}$

$m/z = 31$ $AE = 8.7 \pm 0.2 \text{ eV}$

thermal
decomposition,
photoionization:



M06/6-31+G(d,p)



Conclusions

- Basicity and nucleophilicity of anions in ILs can be predicted using GIL model.
- HNO_3 reacts very rapidly with Cl^- impurity in the ionic liquid to form HCl which vaporizes from the ionic liquid surface rapidly.
- Proton transfer in HEHN confirmed.



Future plans



- Reactive scattering:
 - Obtain higher purity ionic liquid.
- VUV-PIMS:
 - HEHN on catalyst



Acknowledgements



- Ionic Liquids Group:

- Gammy Vaghjiani
- Jerry Boatz
- Tommy Hawkins
- Stefan Schneider



- Leone Group:

- Christine Koh
- Amir Golan
- Oleg Kostko



- Minton Group:

- Vanessa Murray
- Brody Bessire



AFOSR: Mike Berman





Questions?!

