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14. ABSTRACT 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. In complex molecules like RTILs, use of chemical intuition to predict reaction pathways can prove unreliable, especially when the internal energy content is high. There may be concerted reactions that are difficult to predict, and once energy stored in the molecule begins to release, the system does not necessarily follow the minimum energy reaction path, i.e., the subsequent behavior is controlled by dynamics. A useful approach to treating such a system is quasi-classical, direct dynamics trajectory simulations, where the motion of the molecule is followed, allowing the molecule to "show us" what the preferred reaction pathways are. The direct dynamics method dispenses with the potential energy surface. Instead, it calculates the energies, force constants, and Hessian "on the fly" using quantum chemistry methods. This method becomes computationally attractive when the dimensionality of the system increases, particularly for RTILs, which typically contain 10 or more heavy atoms. Dynamics simulations allows the partitioning of the energy generated by exothermic reactions into vibrational, rotational, and translational degrees of freedom, thereby increasing the chance of locating new reaction pathways in the system. In addition, by following the variation of the potential energy during the trajectory rather than relying on intuition, we can identify better geometries for TS searching. Results obtained from these direct dynamics simulations are compared to and consistent with the gaseous products detected experimentally via tunable vacuum ultraviolet photoionization mass spectrometry performed at the Chemical Dynamics Beamline 9.0.2 at the Advanced Light Source. The likely reaction mechanisms in the thermal decomposition of RTILs are discussed in this work.				
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Thermal decomposition mechanisms of ionic liquids by direct dynamics simulations and vacuum ultraviolet photoionization mass spectrometry

Steve Chambreau

*American Chemical Society Spring National Meeting
New Orleans, Louisiana
April 10, 2013*

*ERC, Inc.
Aerospace Systems Directorate
Propellants Branch
Air Force Research Laboratory
AFRL/RQP
10 E Saturn Blvd
Edwards AFB, CA 93524*

Tel: 661 275 6176

Fax: 661 275 5471

Email: steven.chambreau.ctr@edwards.af.mil





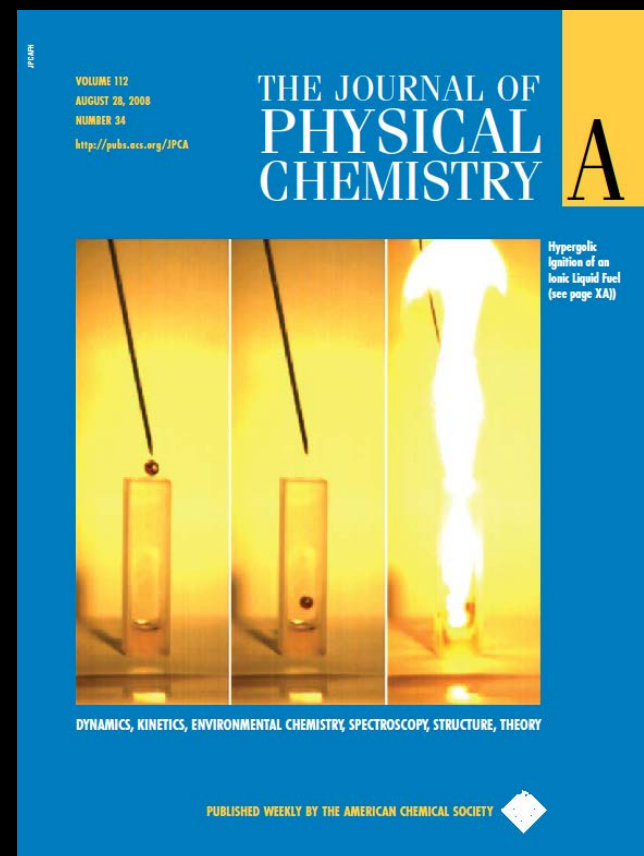
Outline



- Direct dynamics and RRKM modeling of:
 - 1,5-dinitrobiuret (DNB) pyrolysis.
 - EMIM⁺dca⁻, EMMIM⁺dca⁻
- IL vapor studies:
 - Photoionization of vaporized ILs.
- IL aerosols + HNO₃:
 - Diffusion-limited reactivity: MM
- QM/MM reactive scattering:
 - hyperthermal O(³P) off IL surface



What is *hypergolicity*??!



J. Phys. Chem. A, **2008**, 112 (34), pp 7816–7824
DOI: 10.1021/jp8038175



Motivation

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



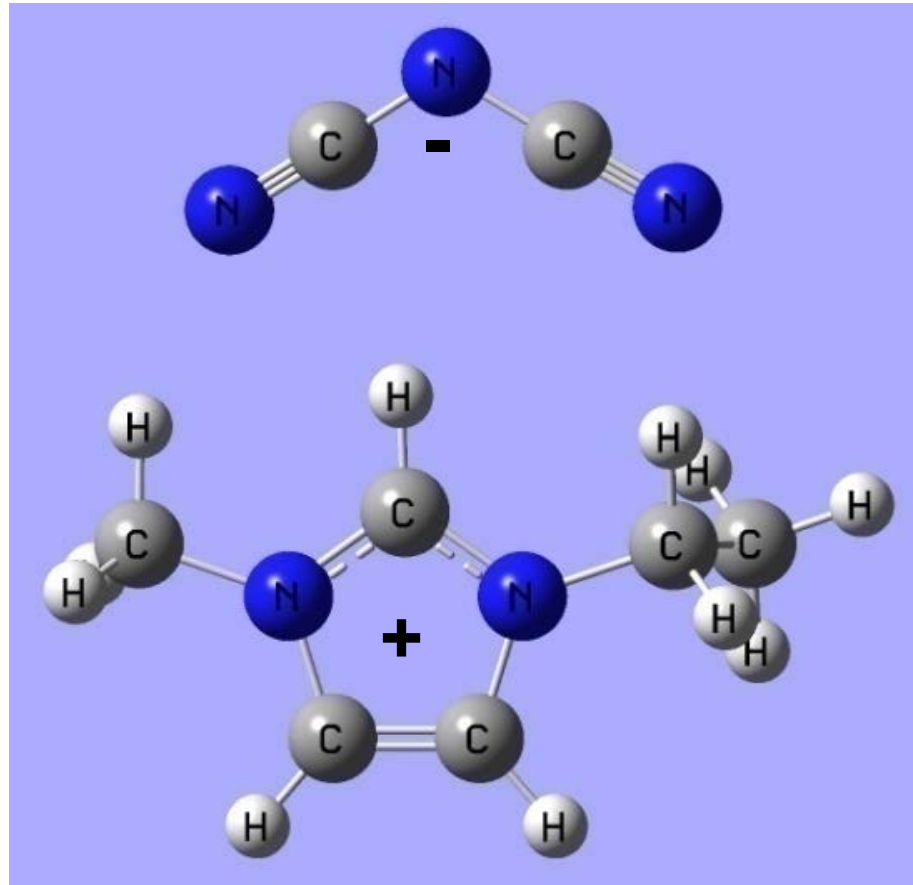


Ionic Liquids

- Molten salts with m.p. ≤ 100 °C.
- Asymmetric ions with diffuse charge distributions.
- C^+A^- : 10^{18} possible combinations of cations and anions.



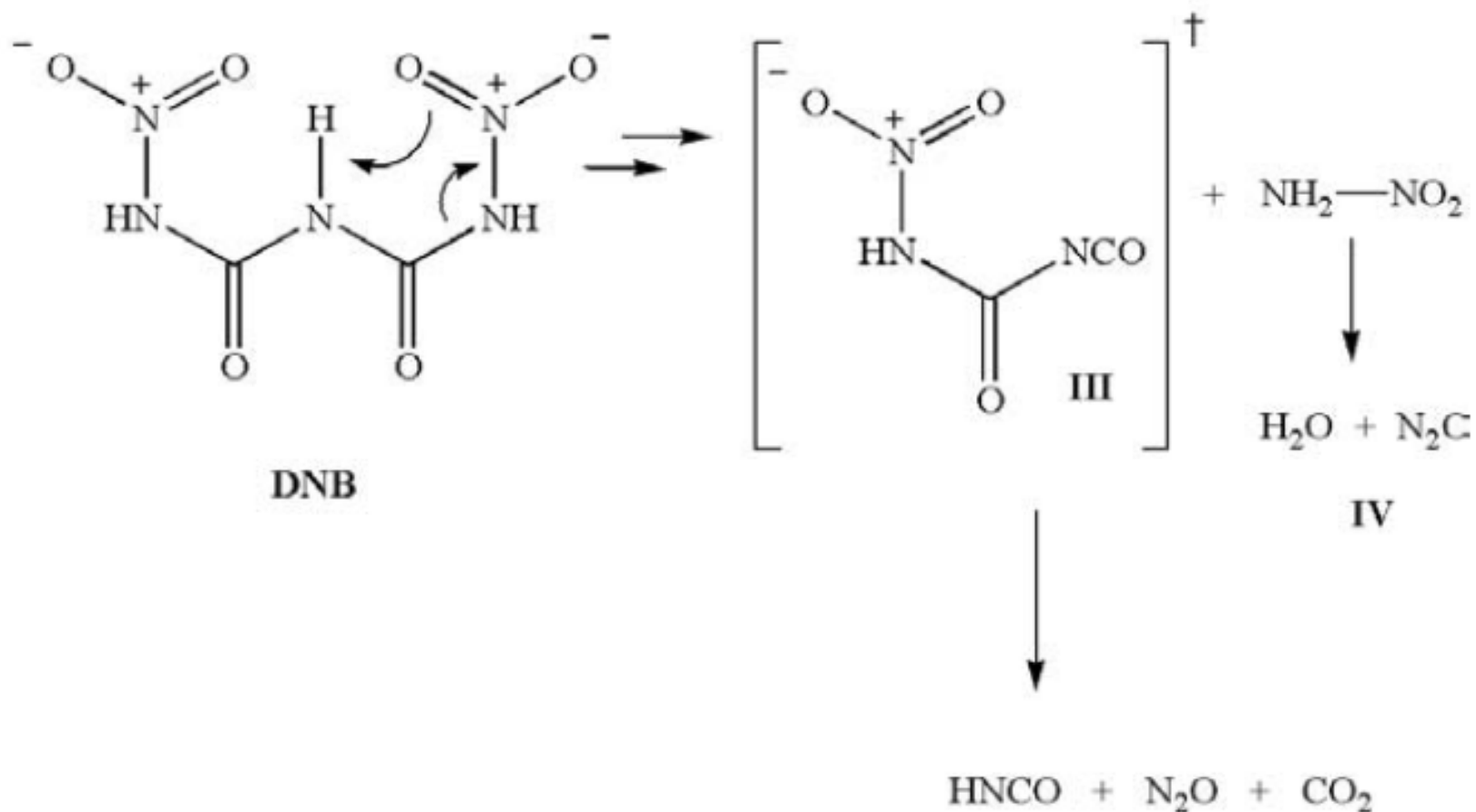
Background



- Dicyanamide-based RTILs first hypergolic ILs discovered with HNO_3 .

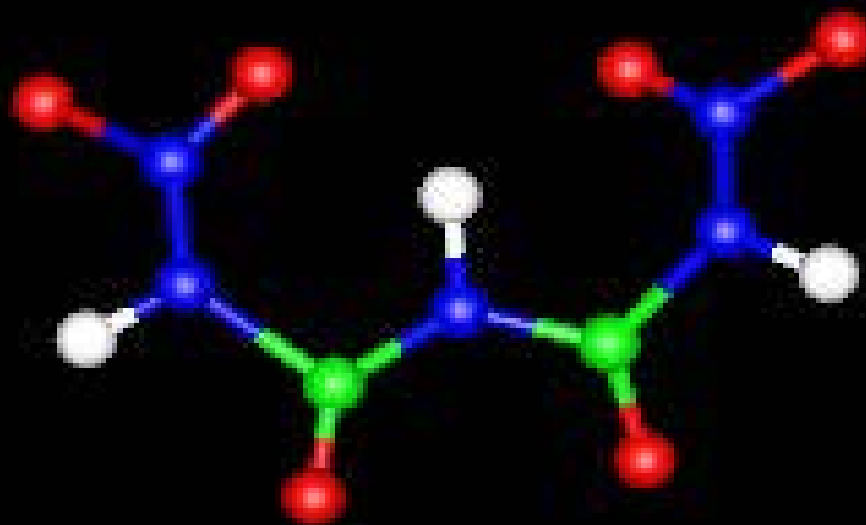


Gas Phase Decomposition of DNB

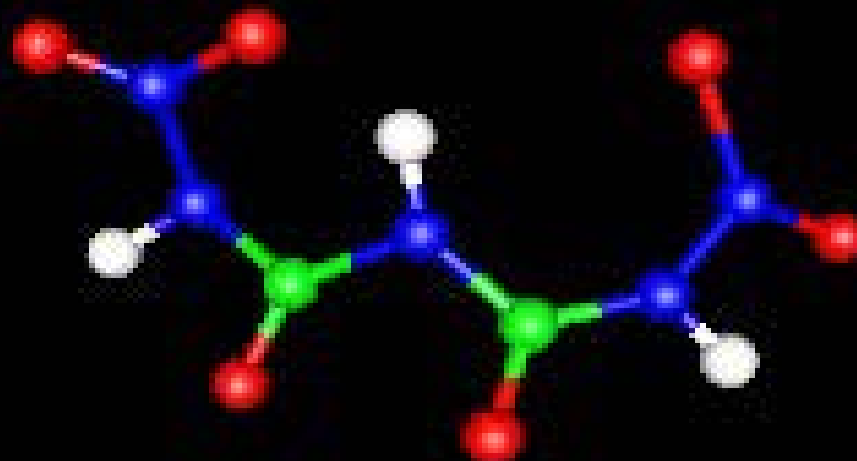


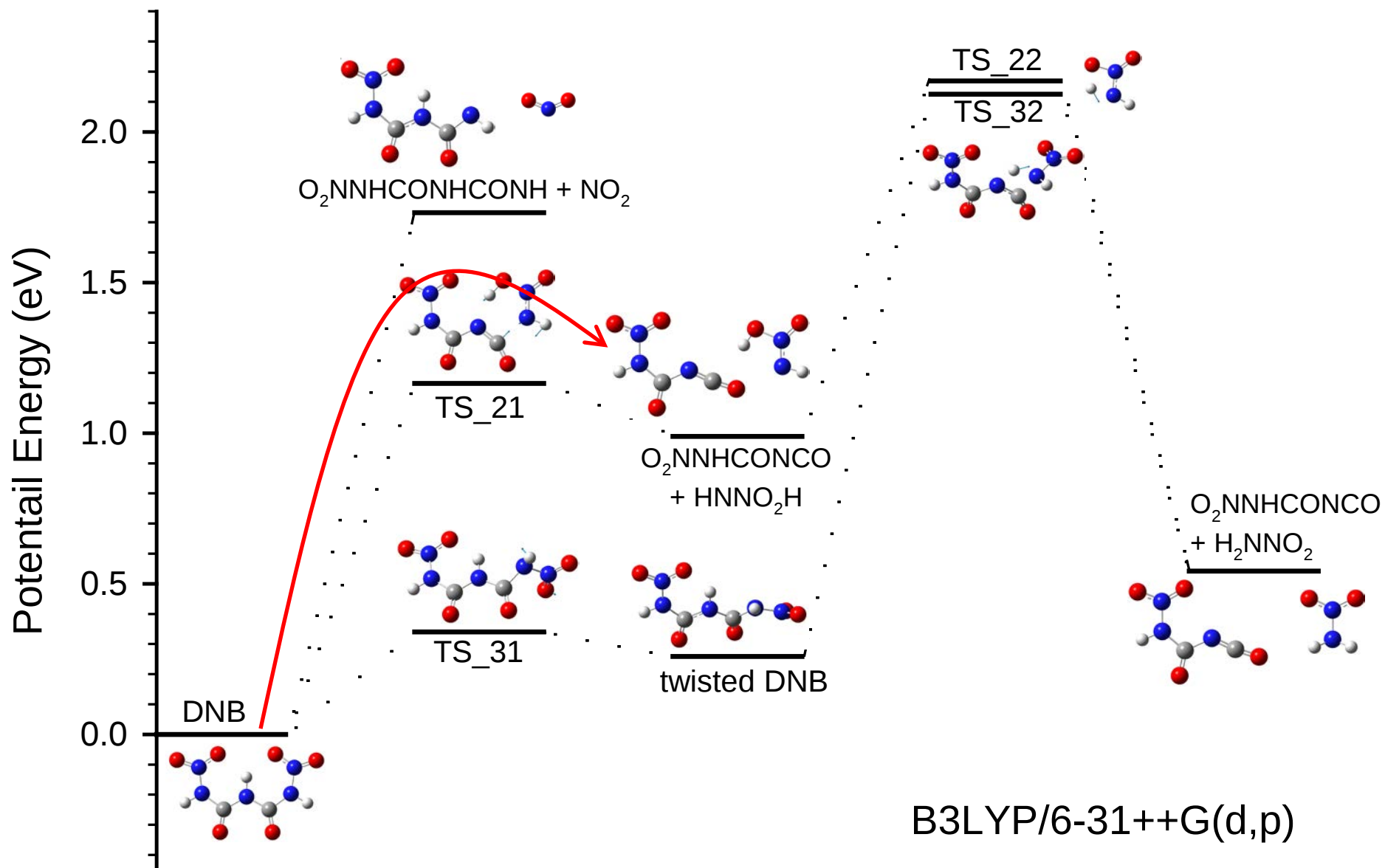
Geith, J., Holl, G., Klapötke, T. M., Weigand, J. J., *Combust. Flame*, **2004**, 139, 358-366

Frame #: 1



Frame #: 1





RRKM Results

Temp / K	750	1000	1250	1500	1750	2000
density of states ($1/\text{cm}^{-1}$)						
DNB	1.95×10^{18}	2.34×10^{22}	5.98×10^{25}	4.94×10^{28}	1.71×10^{31}	2.92×10^{33}
twisted DNB	1.90×10^{18}	2.33×10^{22}	6.04×10^{25}	5.04×10^{28}	1.75×10^{31}	3.02×10^{33}
unimolecular rates (s^{-1}) ^a						
k_1	0 (0)	0.6 (3.6)	1.8×10^4 (1.8×10^5)	2.1×10^6 (2.7×10^7)	3.9×10^7 (5.8×10^8)	2.9×10^8 (4.7×10^9)
k_2	8.5	9.7×10^5	7.9×10^7	1.0×10^9	5.5×10^9	1.8×10^{10}
k_{31}	3.4×10^9	1.5×10^{10}	3.5×10^{10}	6.0×10^{10}	8.8×10^{10}	1.2×10^{11}
k_{31}	2.4×10^{11}	3.2×10^{11}	3.8×10^{11}	4.4×10^{11}	4.8×10^{11}	5.1×10^{11}
k_{32}	0	1.5×10^{-2}	2.1×10^4	7.9×10^6	2.9×10^8	3.4×10^9
branching ratios (%) ^a						
path 1	0	0	0 (0.3)	0.2 (2.6)	0.7 (9.1)	1.3 (18.0)
path 2	100	100	100 (99.7)	99.0 (96.7)	94.3 (86.3)	83.3 (69.2)
path 3	0	0	0	0.8 (0.8)	5.0 (4.5)	15.4 (12.8)

() = loose transition state for path 1



IL Vaporization

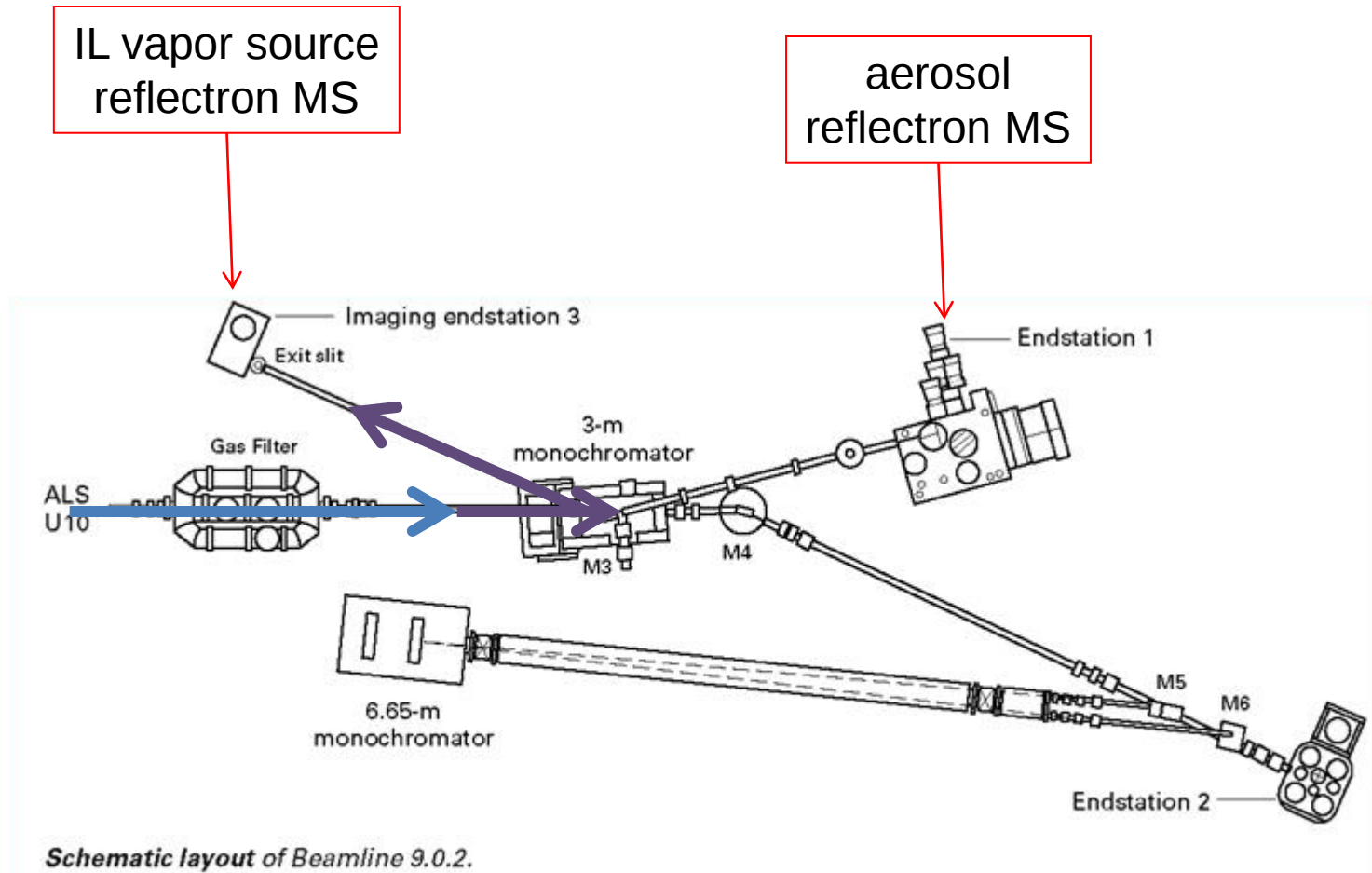
- Strasser, Armstrong, indicate ion pairs by detection of intact cation:¹
 - **Ionic Liquid + $\Delta \rightarrow \text{C}^+\text{A}^-_{(\text{g})}$**
 - **$\text{C}^+\text{A}^-_{(\text{g})} + h\nu \rightarrow \text{C}^+\text{A} + \text{e}^- \rightarrow \text{C}^+ + \text{A} + \text{e}^-$**
- Kelkar and Maginn: ion pairs more energetically favorable than clusters of ion pairs and non-neutral clusters.²

¹ *J. Phys. Chem. A*, 2007, **111**, 3191-3195; *PCCP*, 2007, **9**, 982-990.

² *J. Phys. Chem. B*, 2007, **111**, 9424-9427.



ALS: Chemical Dynamics Beamline

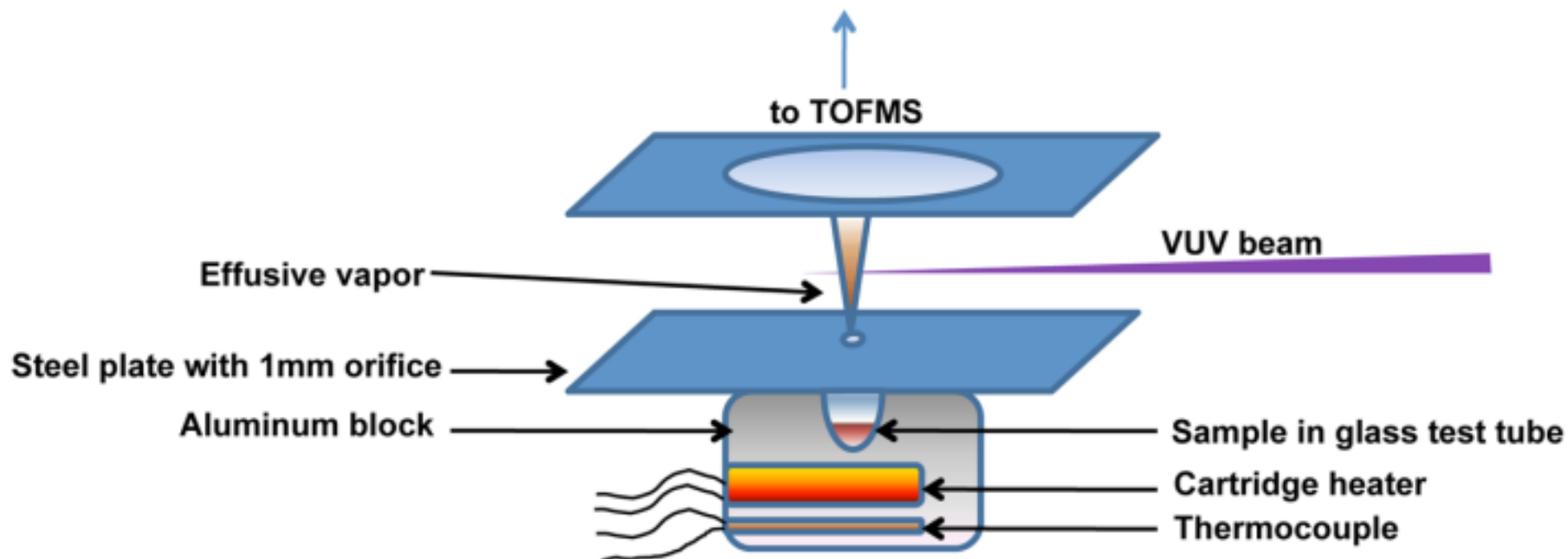


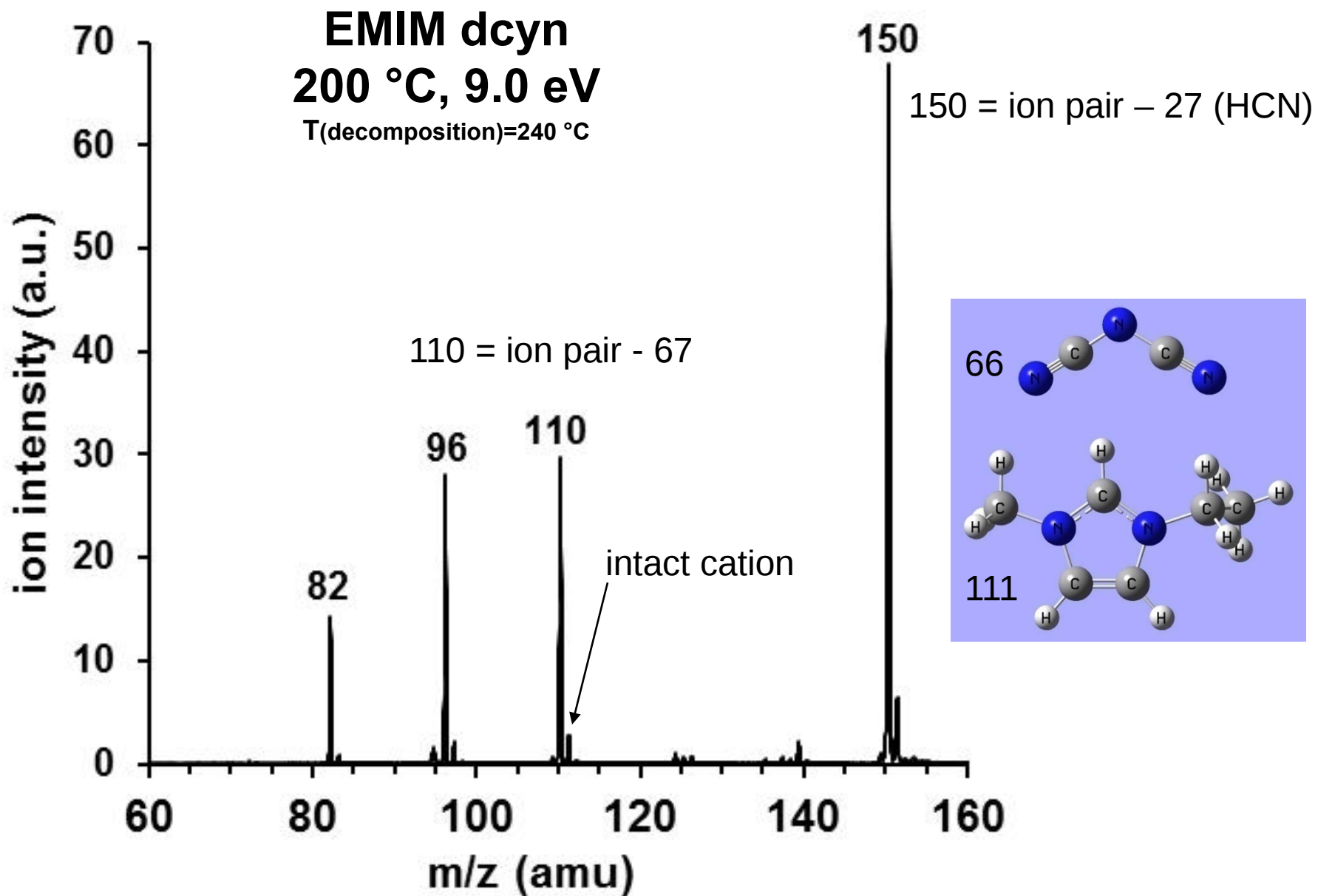
7.4-15.0 eV photons, 0.025 eV resolution



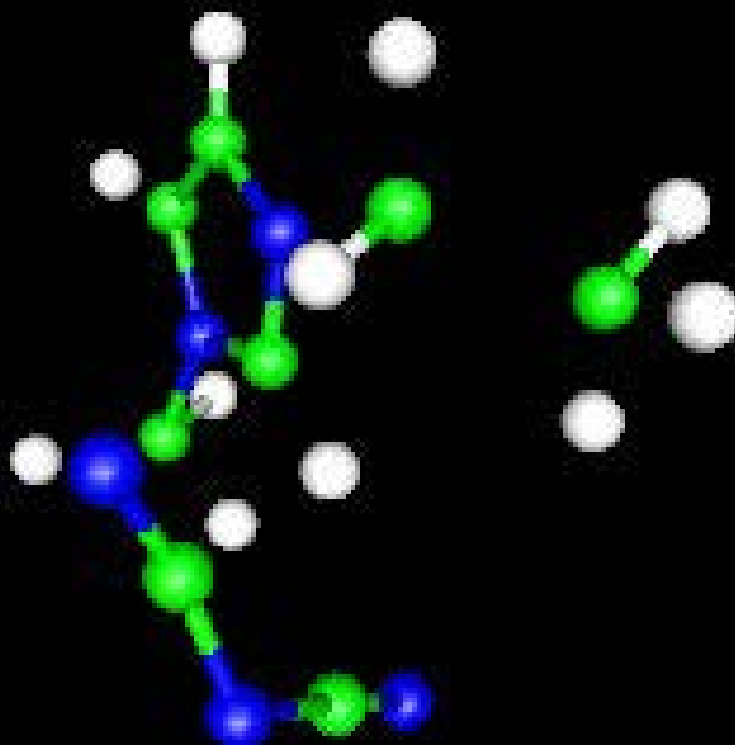
Experimental

IL effusive source:

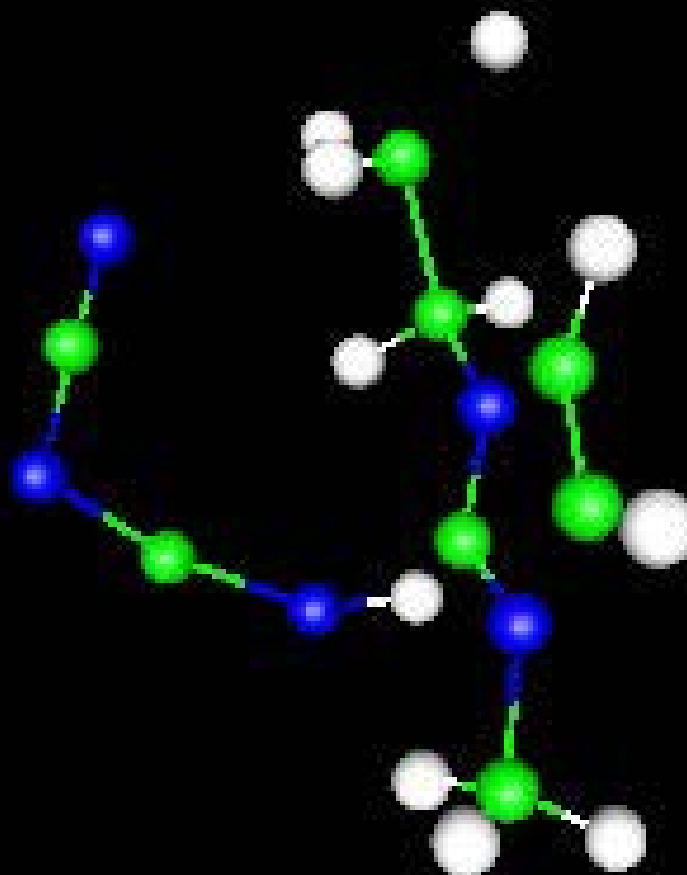




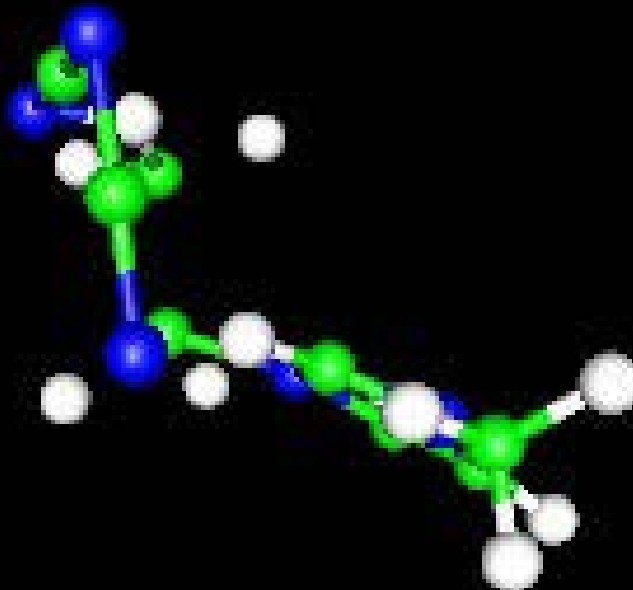
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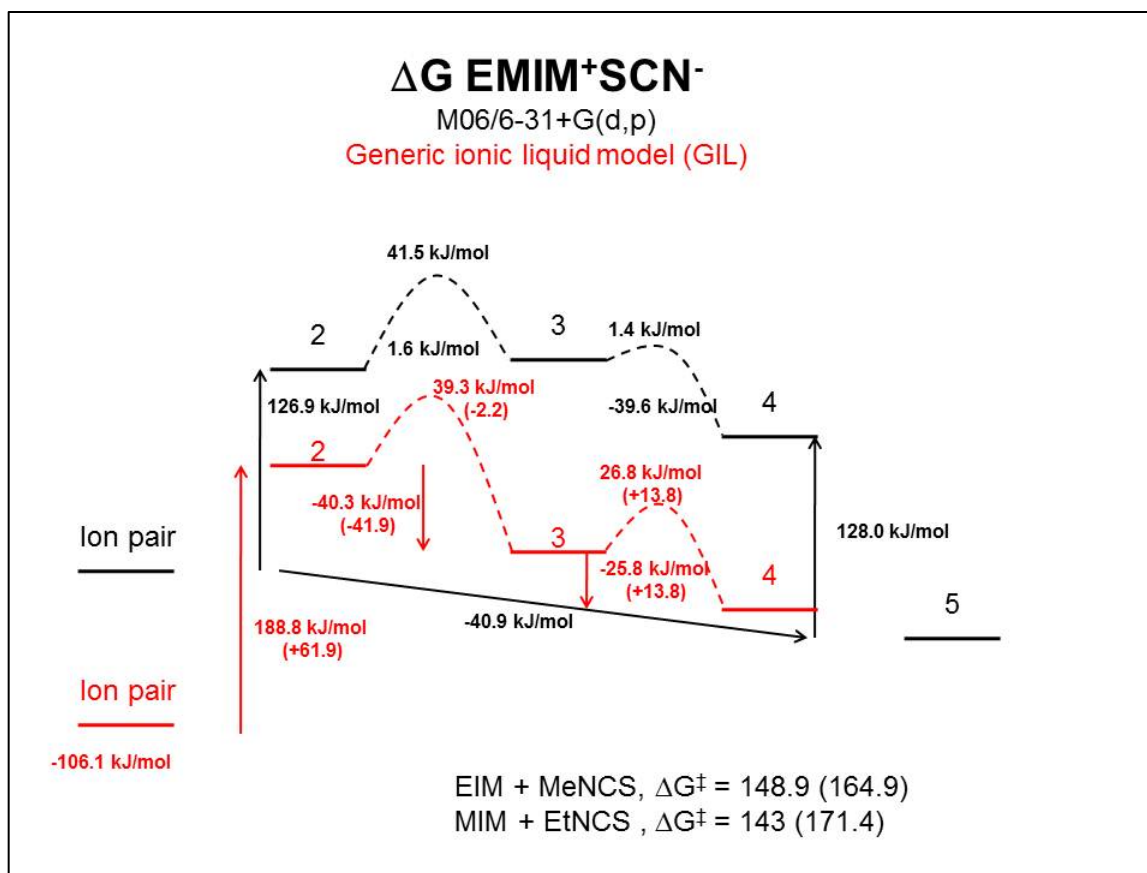
EMIM⁺dca⁻ MD results

MD reaction	# of trajectories	branching ratio (%)
C2 H+ xfer to dca (term)	16	25
C2H5 dissoc	11	17
NCN + CN	8	13
dca dissoc	4	6
NR	4	6
dca abstract H from CH3 --> Hdca (term)	3	5
C2 H+ <-> dca (central)	2	3
CH3 dissoc	2	3
Et: CH3CH2- + dca --> CH2CH2 + Hdca (term)	2	3
H2 elim from -CH3	2	3
NCN-CN elongation	2	3
-C2H5 + dca <--> -C2H4 + Hdca	1	2
C2H5 abstraction by dca (term)	1	2
C2H5 and dca dissoc	1	2
C4H xfer to N3 and elim HC4C5	1	2
CH3 abstraction by dca (central)	1	2
CH3 abstraction by dca (term)	1	2
Et: H2 + dca --> HCN + HNCN	1	2
total=	63	

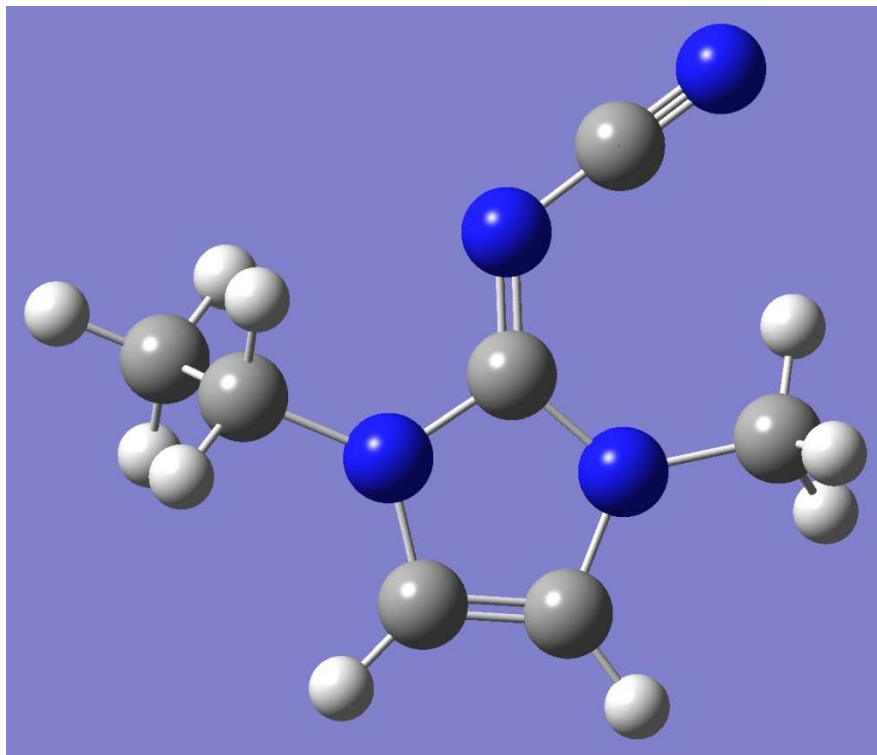


PCM Model for ILs

- Truhlar: SMD-GIL (generic ionic liquid)*
 - benchmark to experimental ΔG_{solv} for ILs.



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

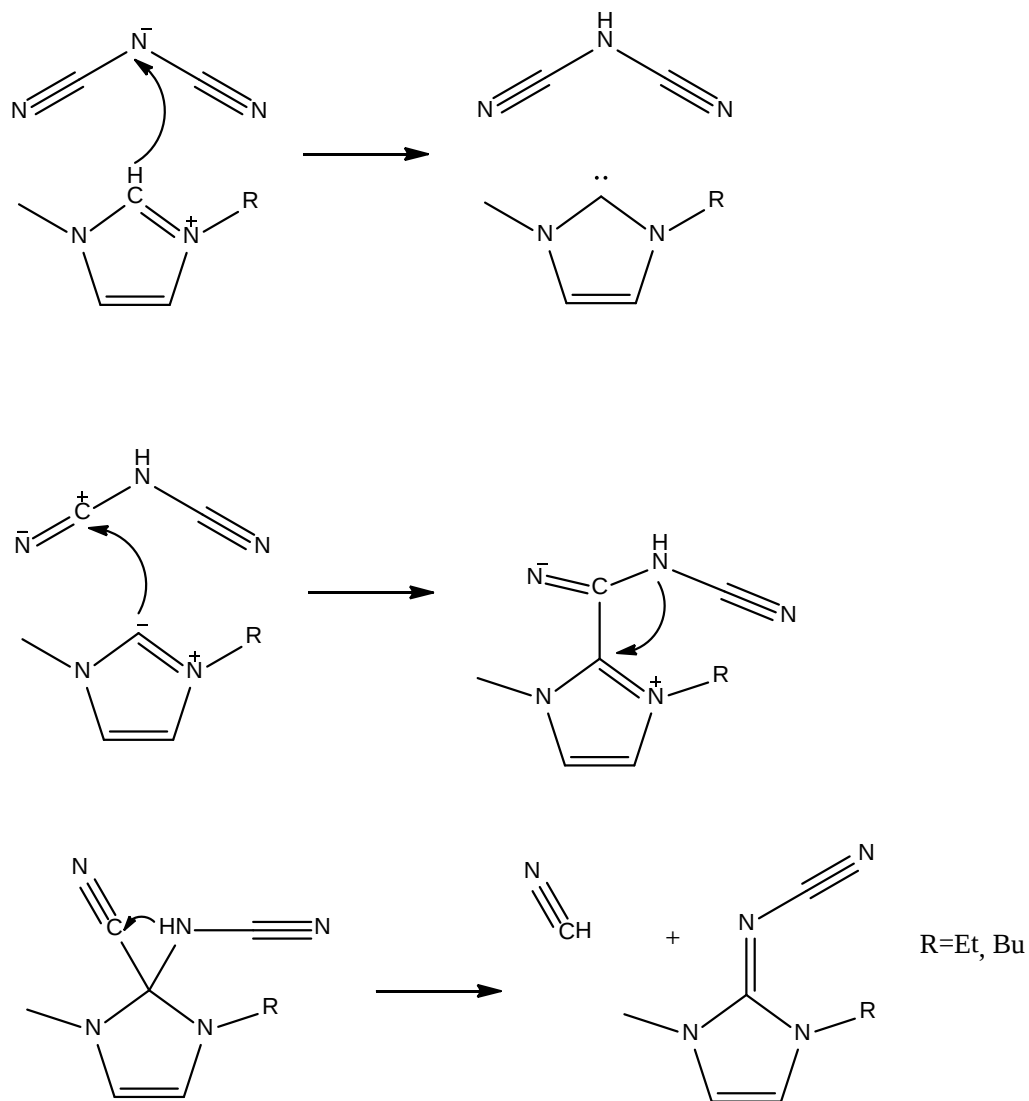


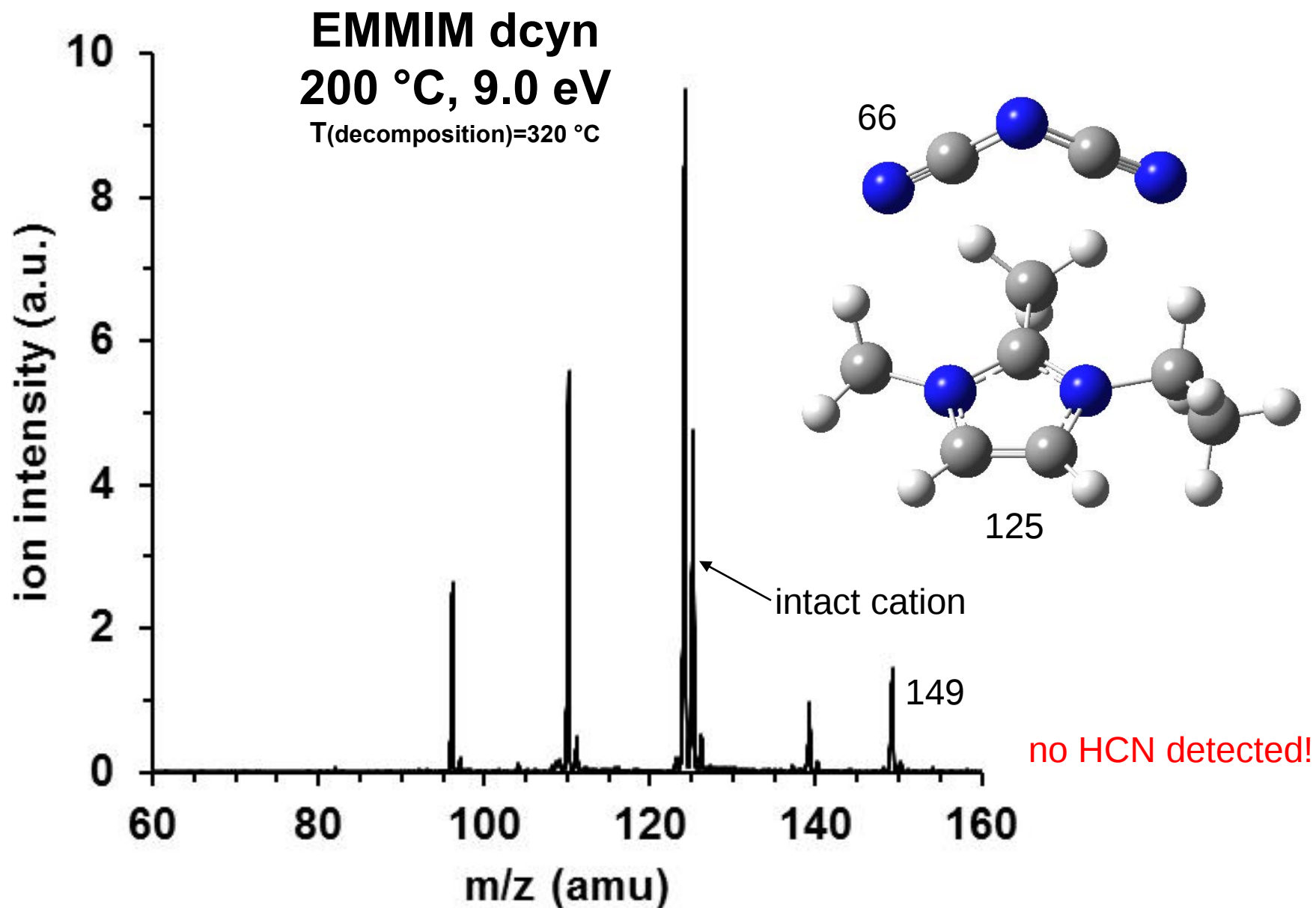
+ HCN

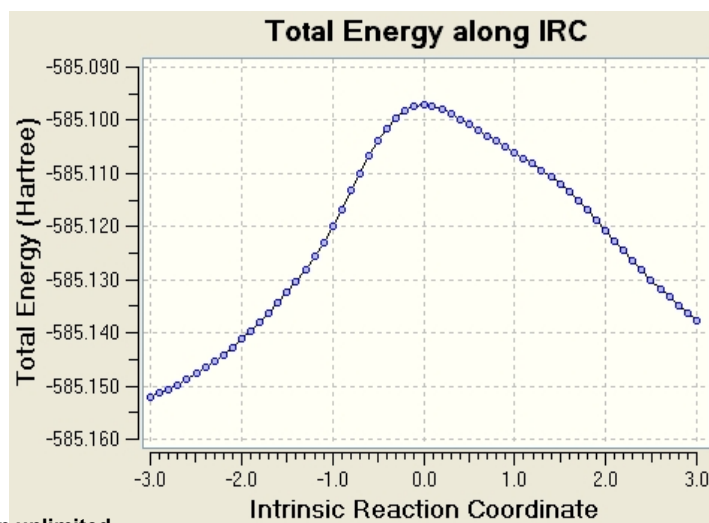
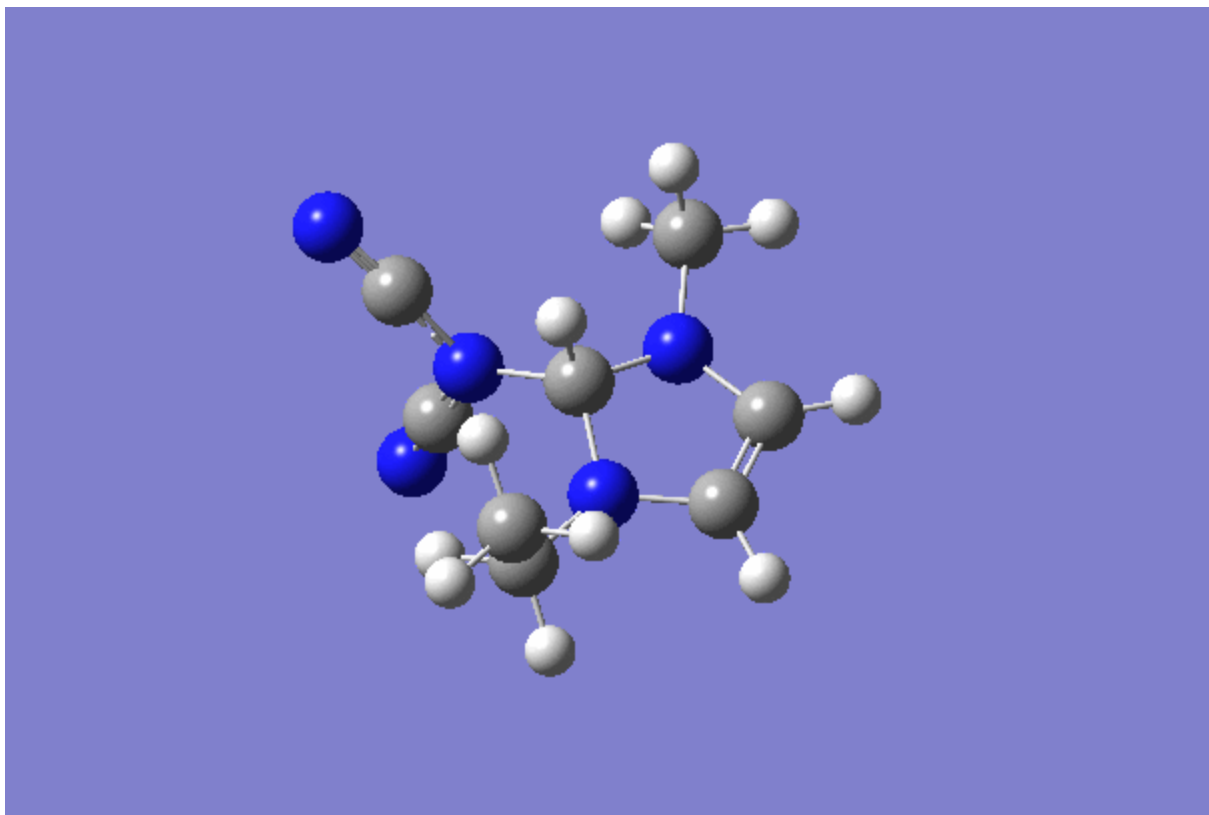
$$\begin{aligned} &\text{Mass 150} \\ &= (111 - 1) + 40 \end{aligned}$$

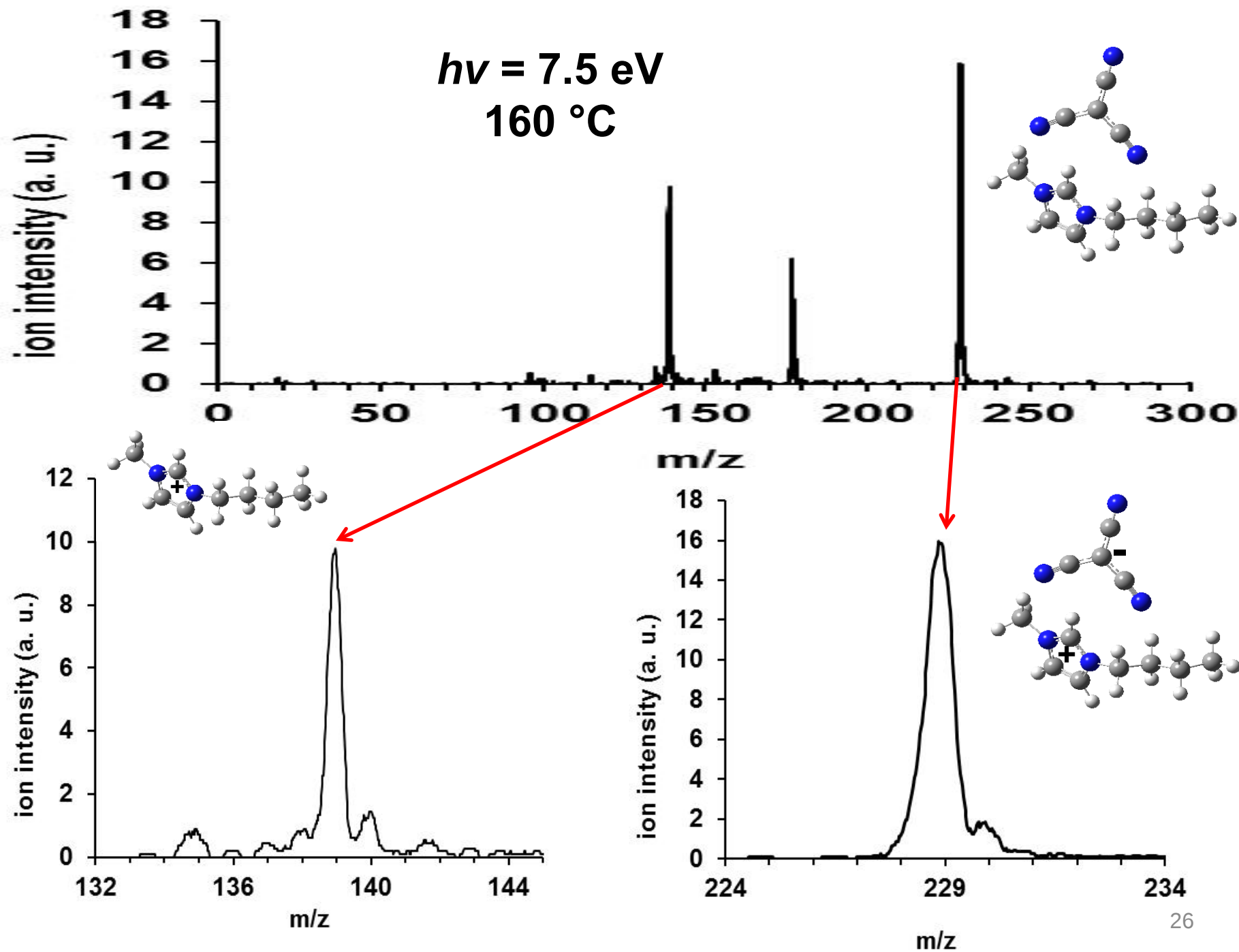


addition-elimination mechanism



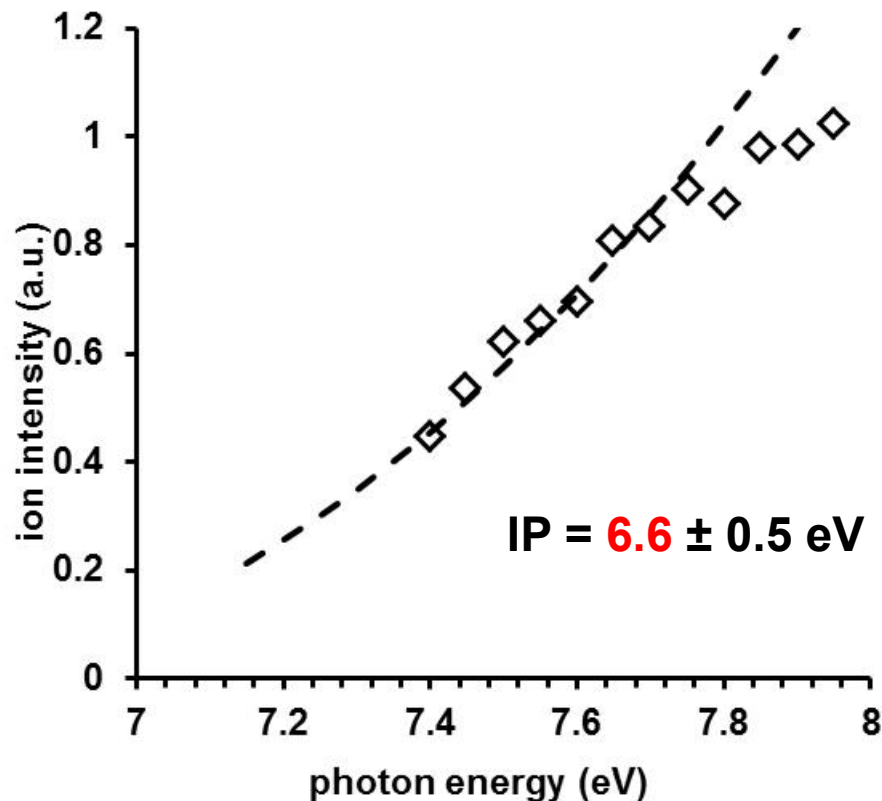
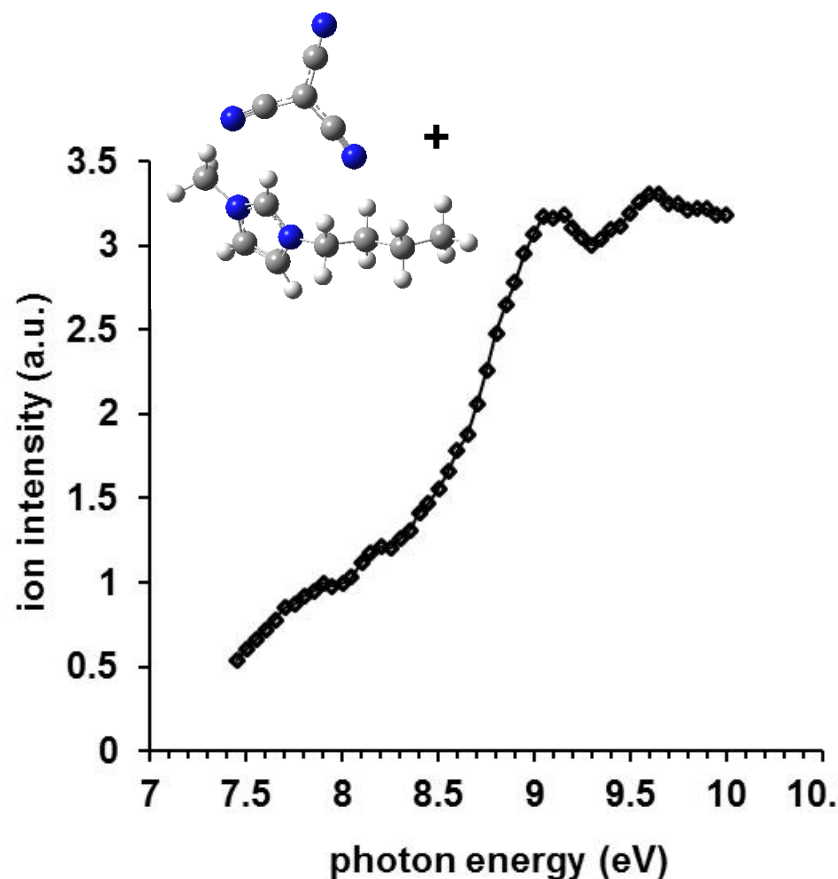








photoionization efficiency of ion pair



J. Phys. Chem. Lett., **3**, 2910 (2012)

IP (M06/6-31+G(d,p))
 7.3 ± 0.2 eV



Aerosol reactivity



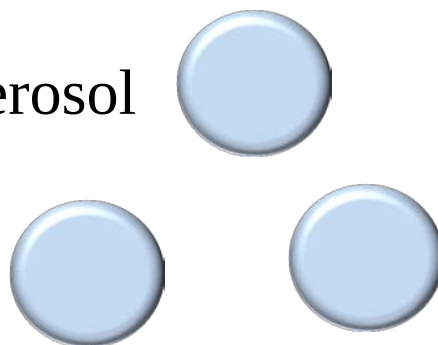
- RTILs very low vapor:
 - Aerosols are liquid droplets suspended in gas phase.



Monitoring isolated ion pairs

- Use it **to study reaction kinetics** of ‘hypergolic ionic liquid reaction with an oxidizer’

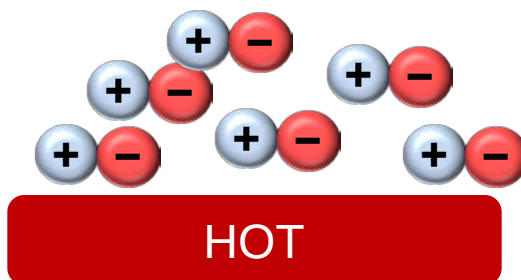
Hypergolic
Ionic liquid aerosol



Hypergolic
Ionic liquid aerosol ‘reacted’

+ $h\nu$

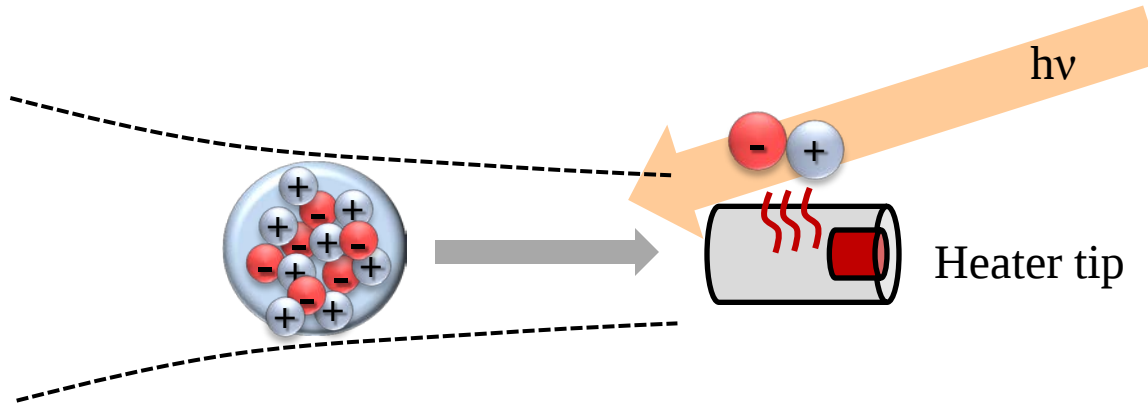
Reaction dynamics
and kinetics



C. J. Koh, et al., *Soft ionization of thermally evaporated hypergolic ionic liquid aerosols*, J. Phys. Chem. **115**, 4630 (2011).



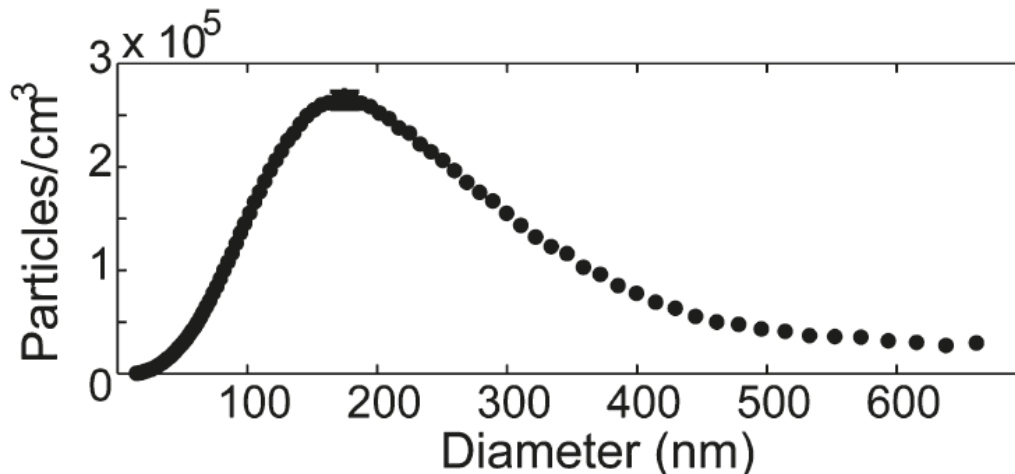
Ionic liquid aerosol generation



- Tunable light source

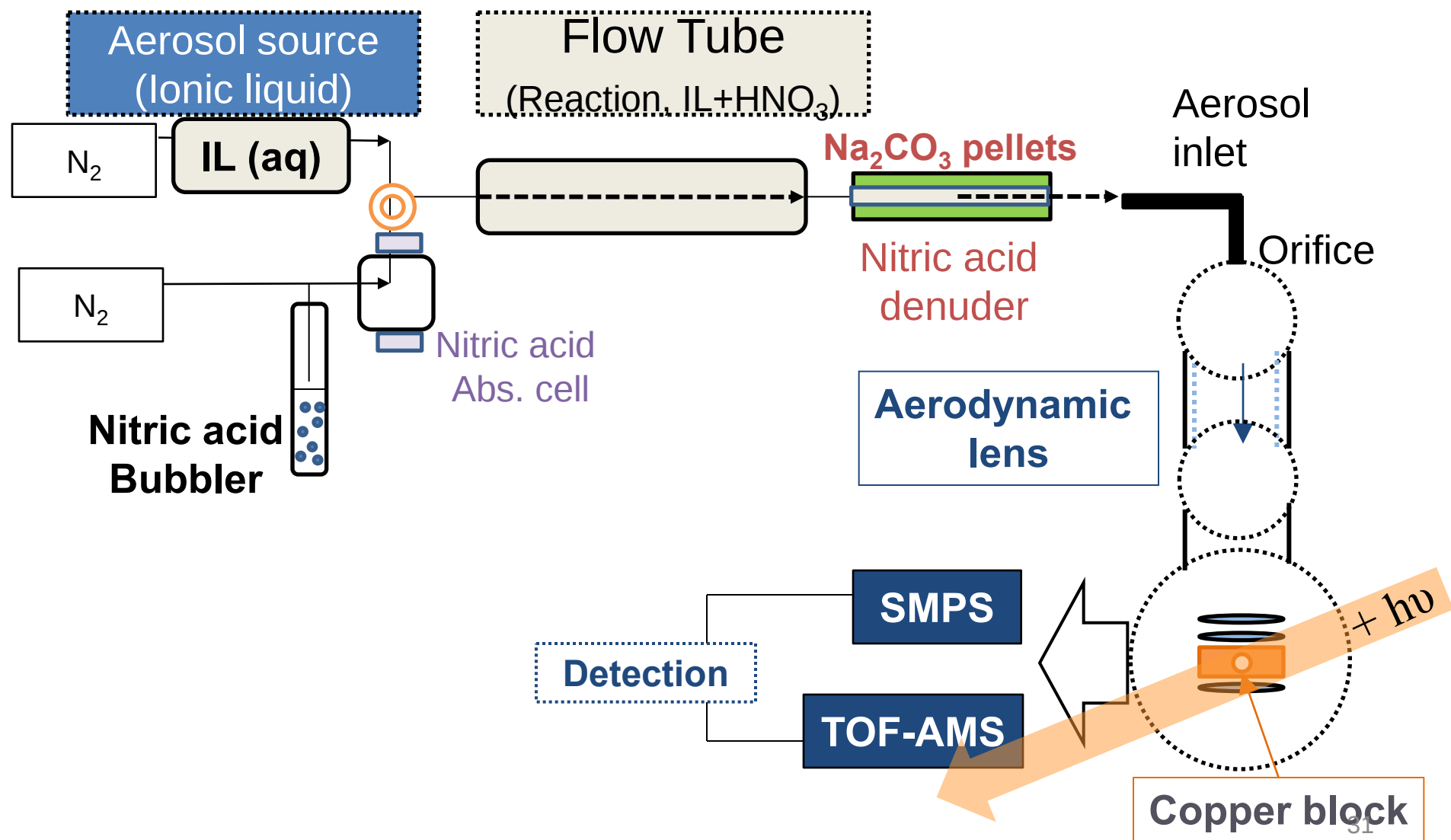
Hypergolic Ionic liquid aerosol

- size distribution





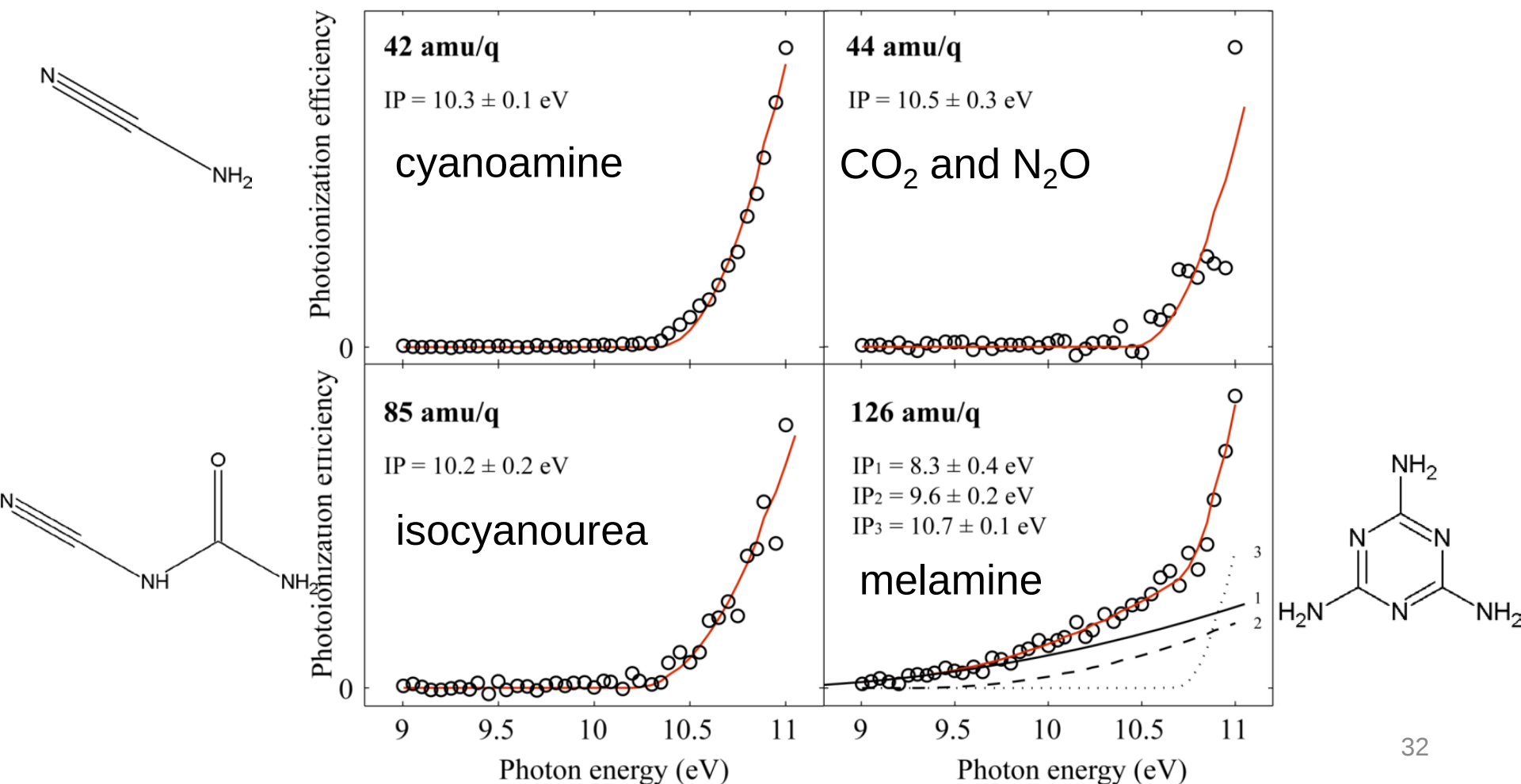
Experimental setup

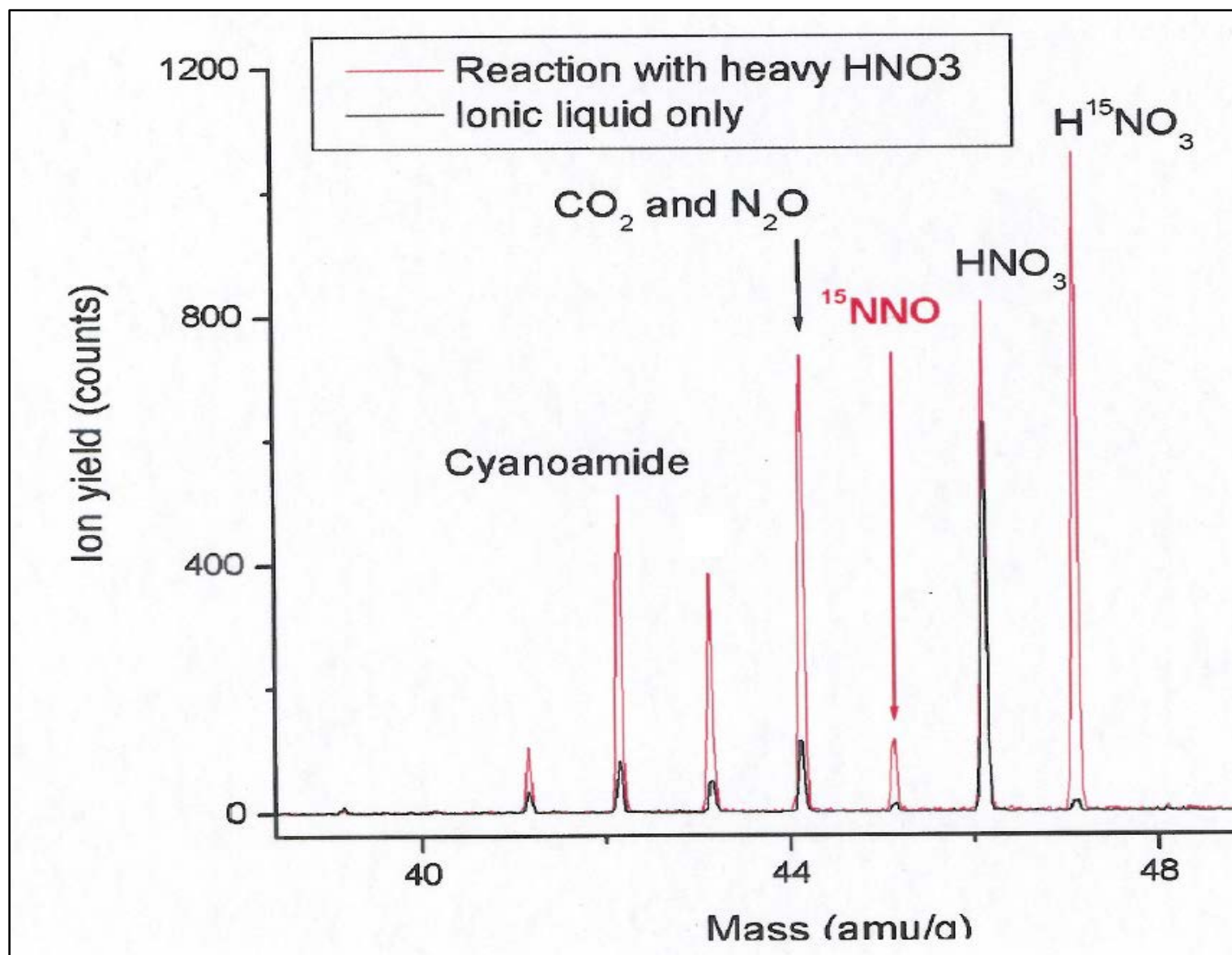




Identification of reaction products

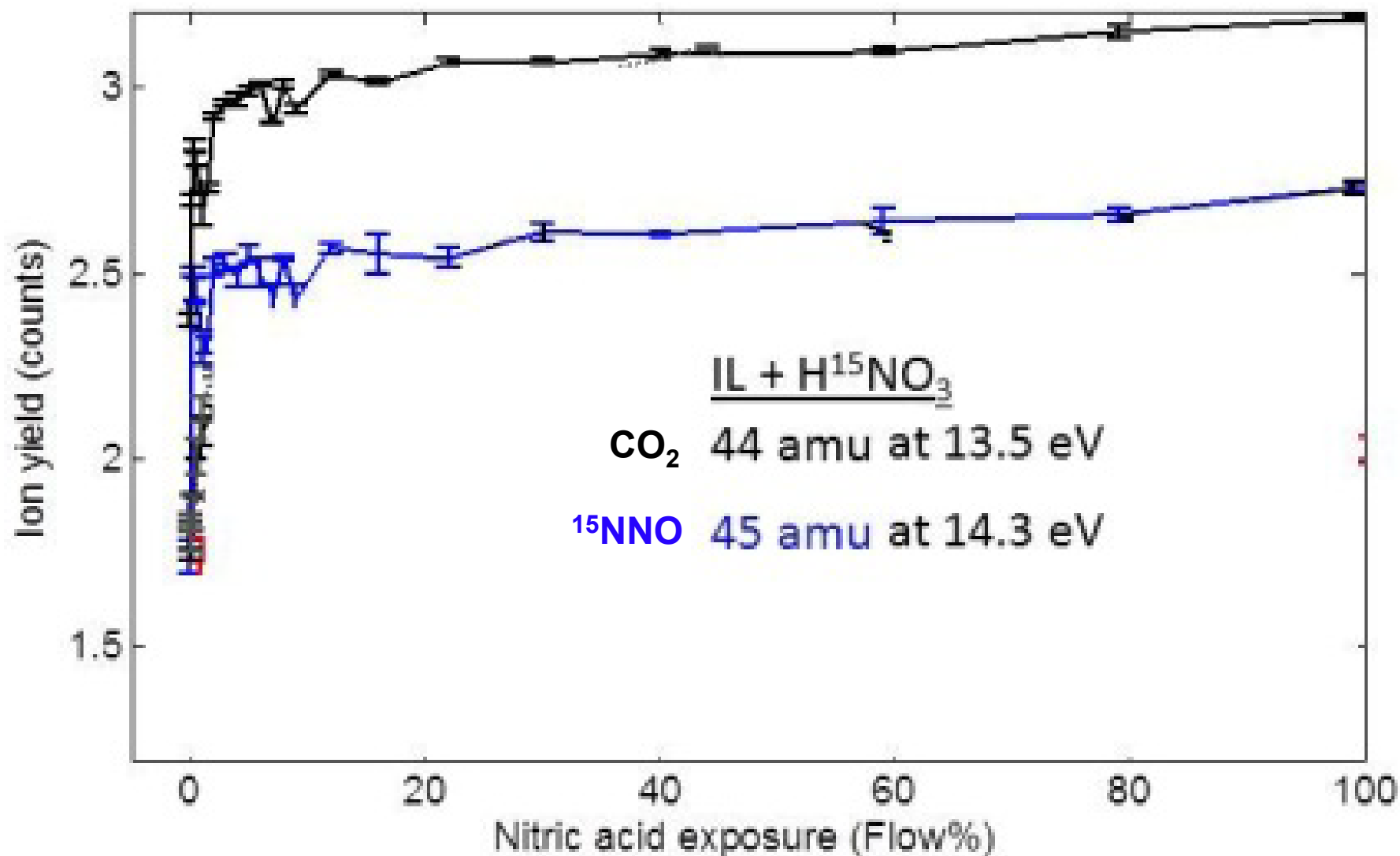
- photoionization efficiency curve measured





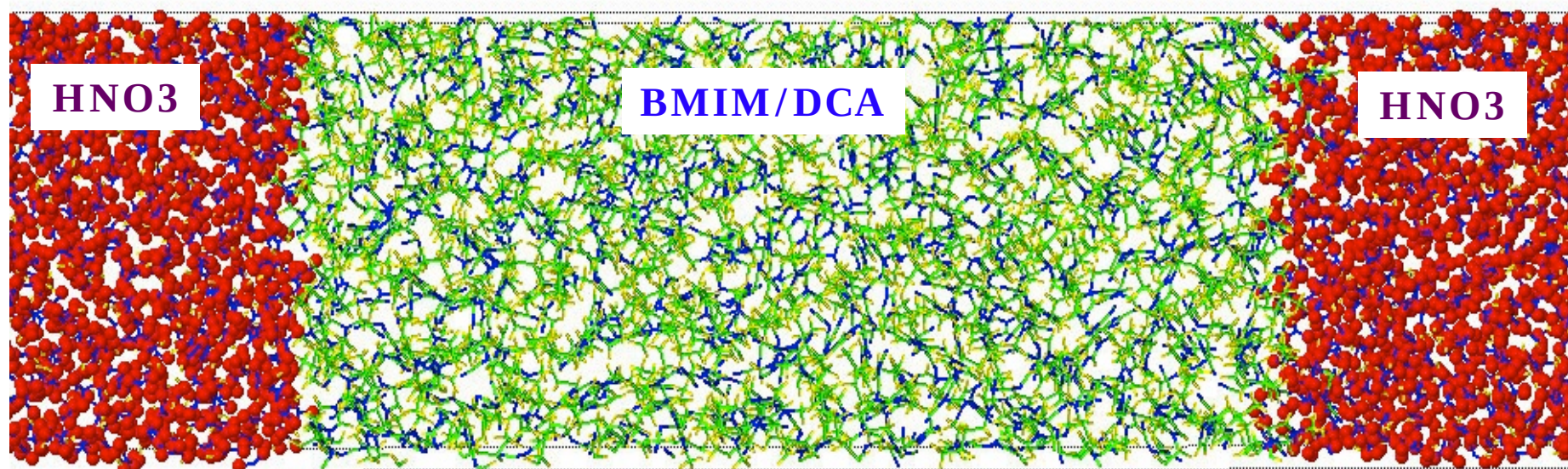


aerosol kinetics data

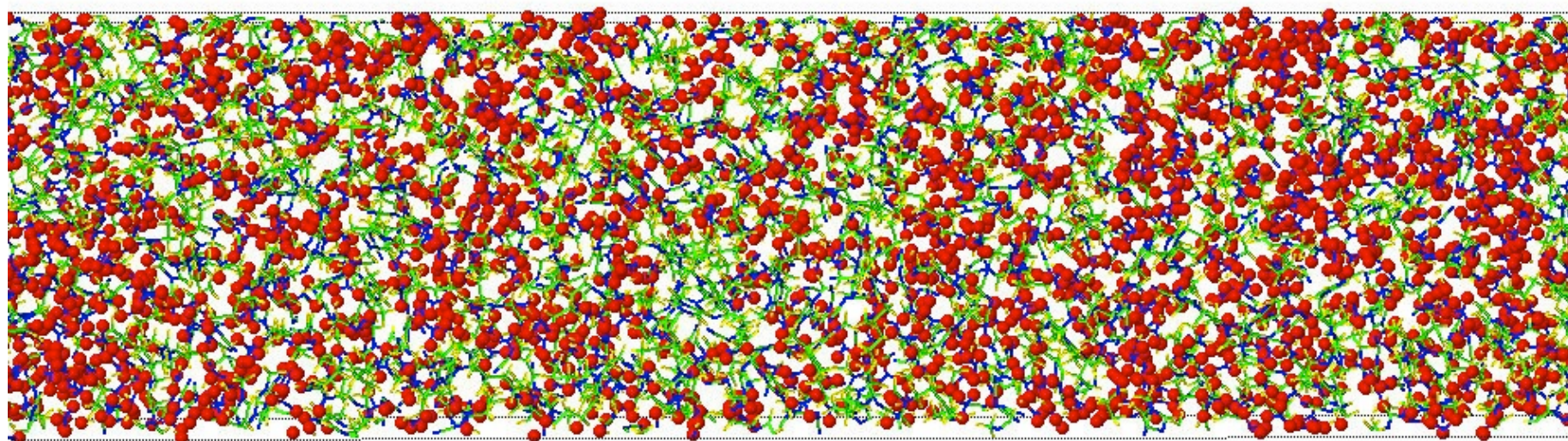


MD simulations of IL/oxidizer interphases: liquid-liquid

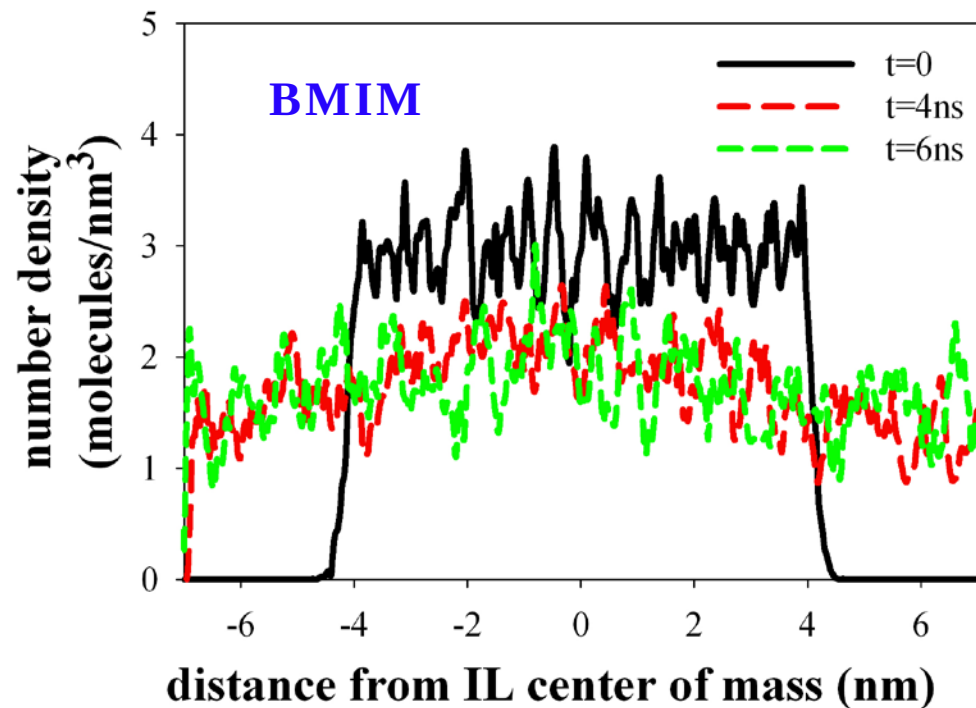
t=0



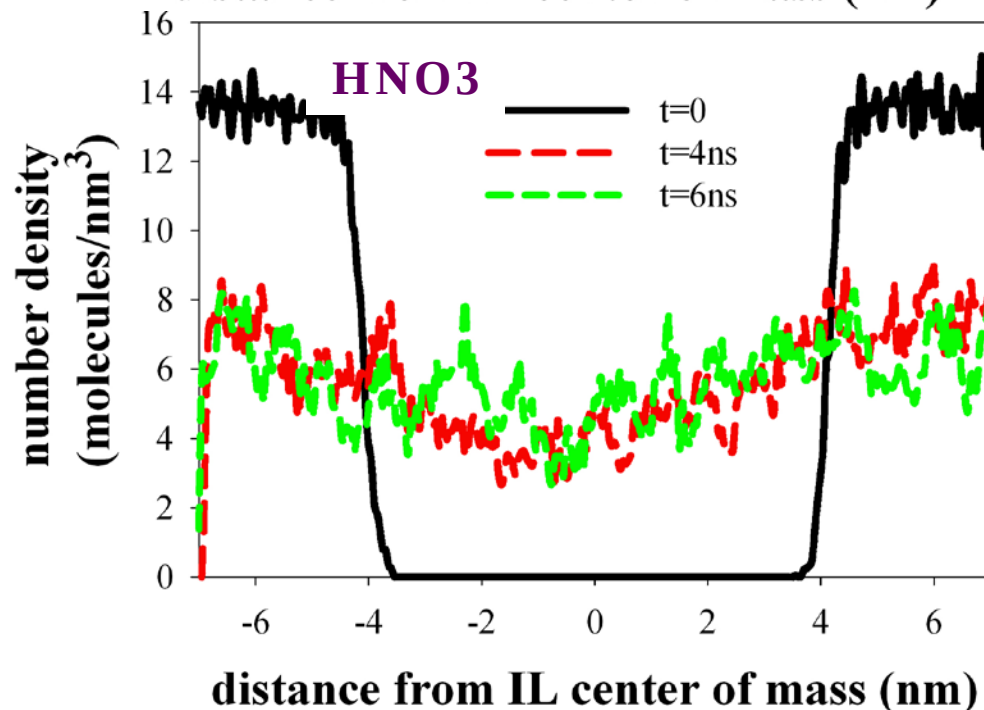
t=6 ns



in liquid/liquid systems, mixing is rapid!

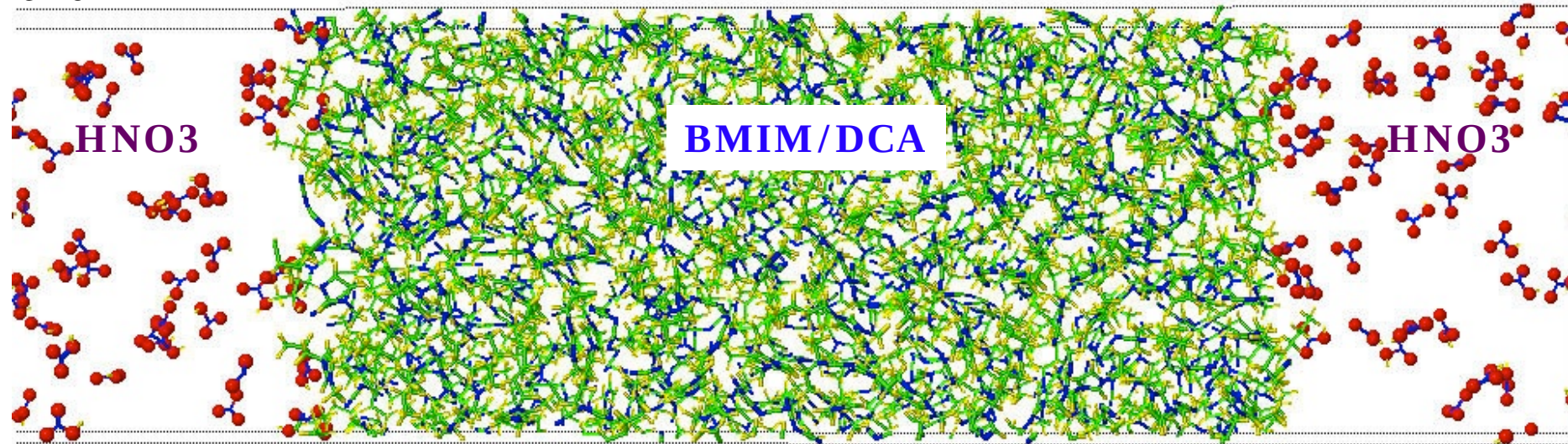


For the liquid-liquid interphase intermixing occurs fast (few ns time scale for investigated dimensions).

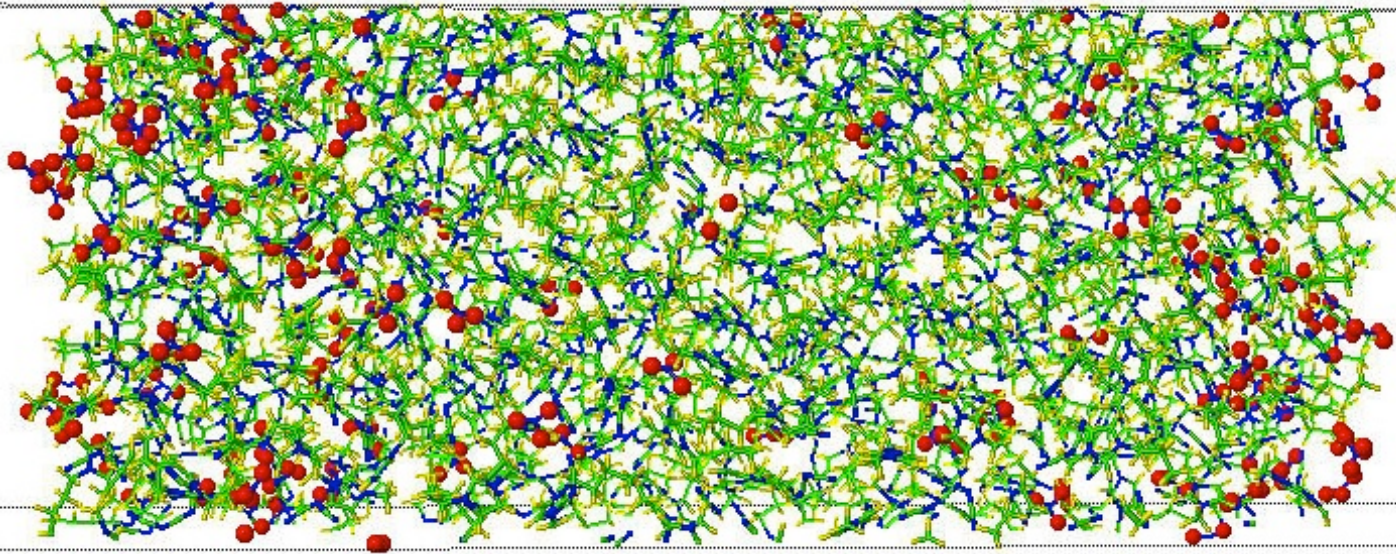


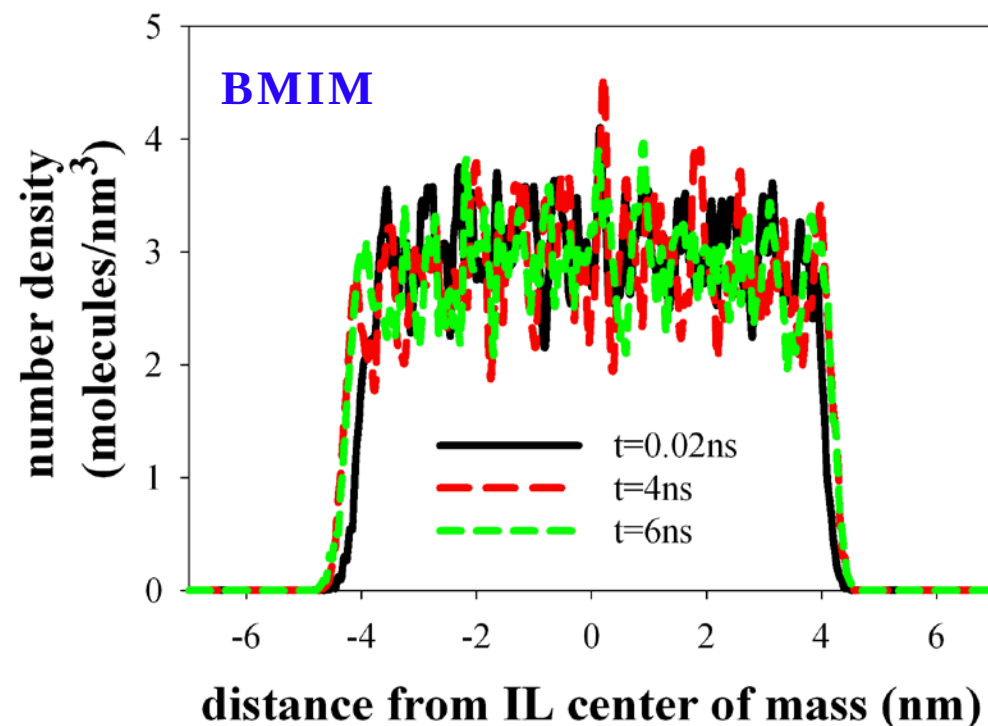
MD simulations of IL/oxidizer interphases: liquid-gas

$t = 0$



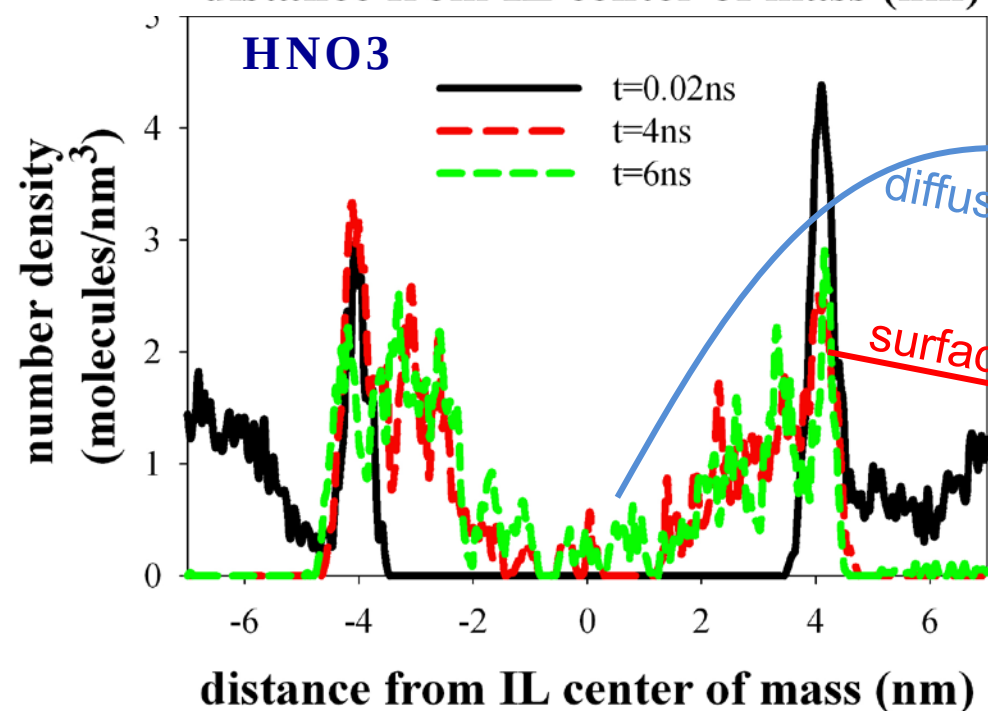
$t = 6 \text{ ns}$





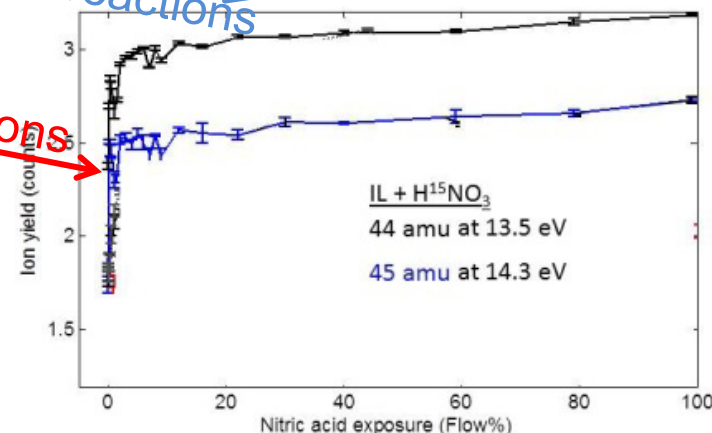
At the liquid-gas interphase HNO₃ quickly adsorbs to the surface and then slowly diffuses to the bulk.

There is a certain concentration of HNO₃ at the surface that system would like to maintain to reduce the surface tension



diffusion-limited reactions

surface reactions





Conclusions

- Molecular dynamics can greatly improve our understanding of reactivity of ionic liquids:
 - ID thermal decomposition mechanisms
 - surface tension/diffusion limited processes
- Tunable VUV-PI-TOFMS a powerful experimental tool:
 - Direct detection of ion pairs upon vaporization
 - ID products by mass *and* ionization potential
 - Aerosols make ionic liquids more accessible by MS
- Design a better green rocket fuel with ionic liquids !!!





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 - Lt. Anna Sheppard



Questions?!



