How hot are your ions in Differential Mobility Spectrometry?

Christian Ieritano, Joshua Featherstone, Alexander Haack, Mircea Guna, J. Larry Campbell, W. Scott Hopkins

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WOH pm 03:50

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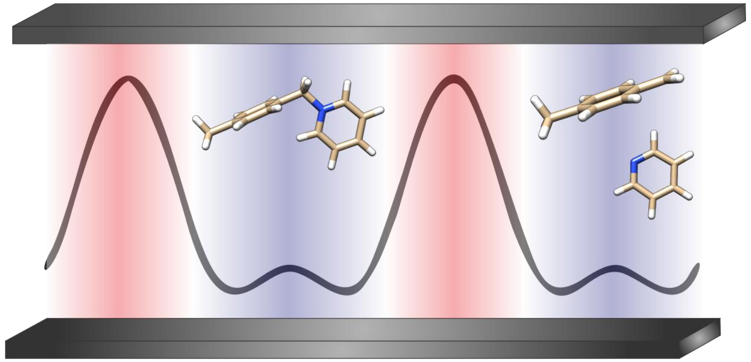
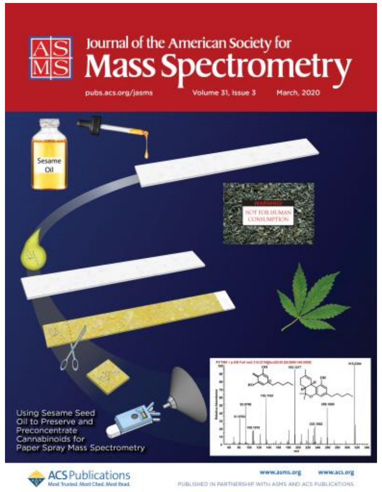
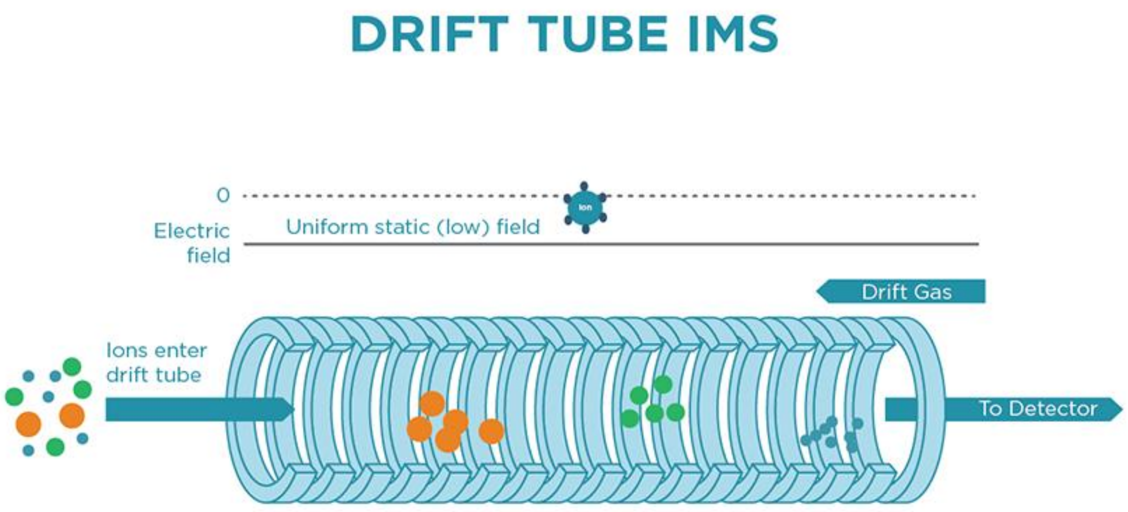
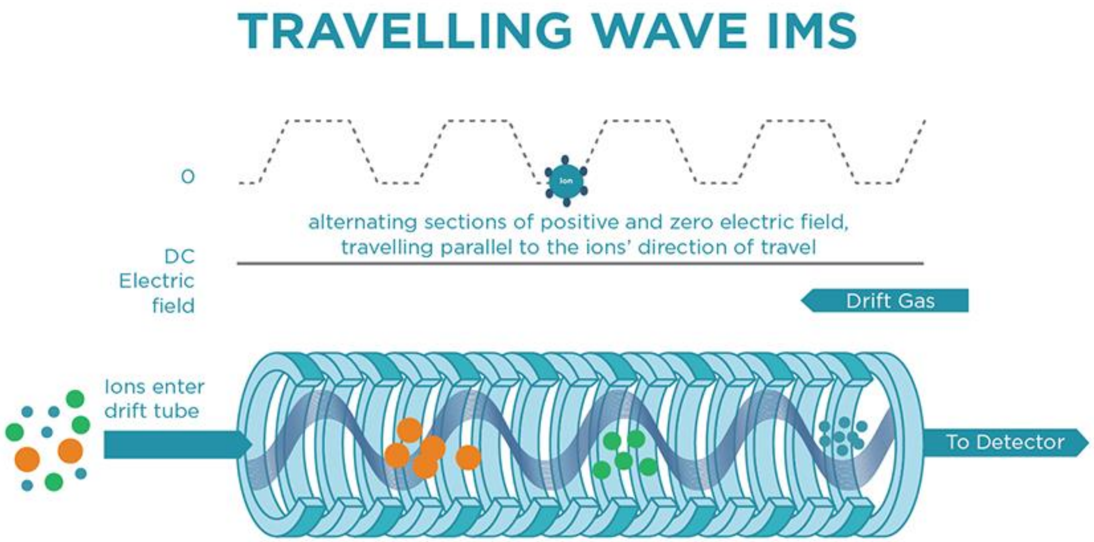




Why is ion heating important?

Ion mobility is our eye into the gas-phase structure of ions.





Direct correlation to ion structure (CCS)

Time dispersive

Ambient pressure (~ 1 bar)

Uniform low $\vec{E}$ (<10 Td)

Empirical relationship with ion structure (CCS)

Time dispersive

Low pressure (0.025 – 3 mbar)

Moving and variable low $\vec{E}$ (> 10 Td)

Figures courtesy of Owlstone Medical

Why is ion heating important?

Structure of gas-phase ions depend on their thermally accessible conformations.

DRIFT TUBE IMS

$$v_d = KE = K_0 N_0 \left(\frac{E}{N}\right)$$

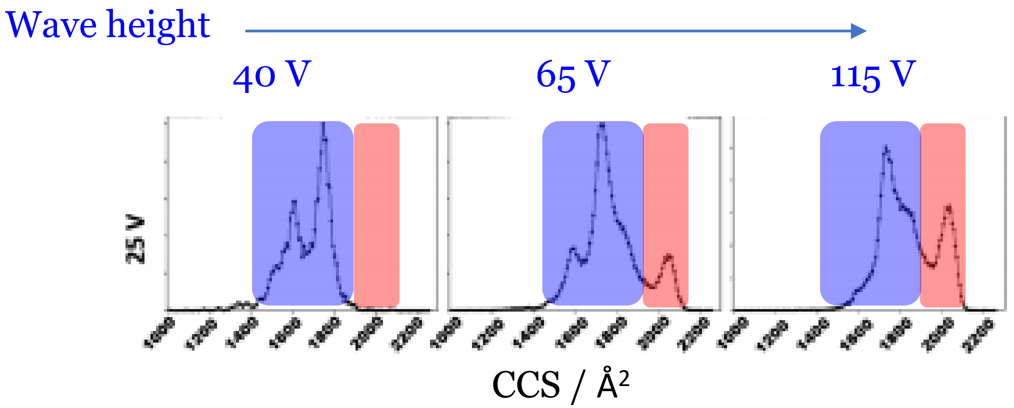
Thermal velocity <<< drift velocity

$$K = \frac{\sqrt{18\pi}}{16}\sqrt{\frac{1}{m_{ion}} + \frac{1}{m_{gas}}}\frac{ze}{\sqrt{k_b T}}\frac{1}{\Omega}\frac{1}{N}$$

Ion heating insignificant

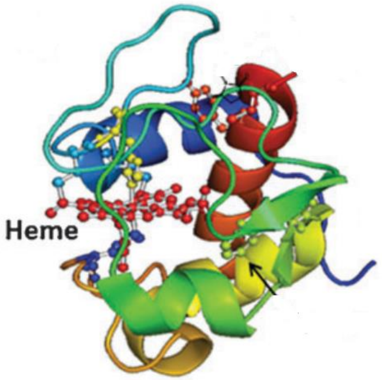
Mason-Schamp valid

TRAVELLING WAVE IMS

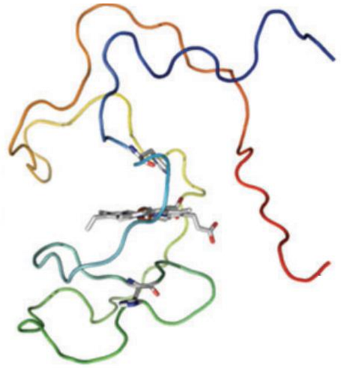


Elongation increases with **wave height**

Compact



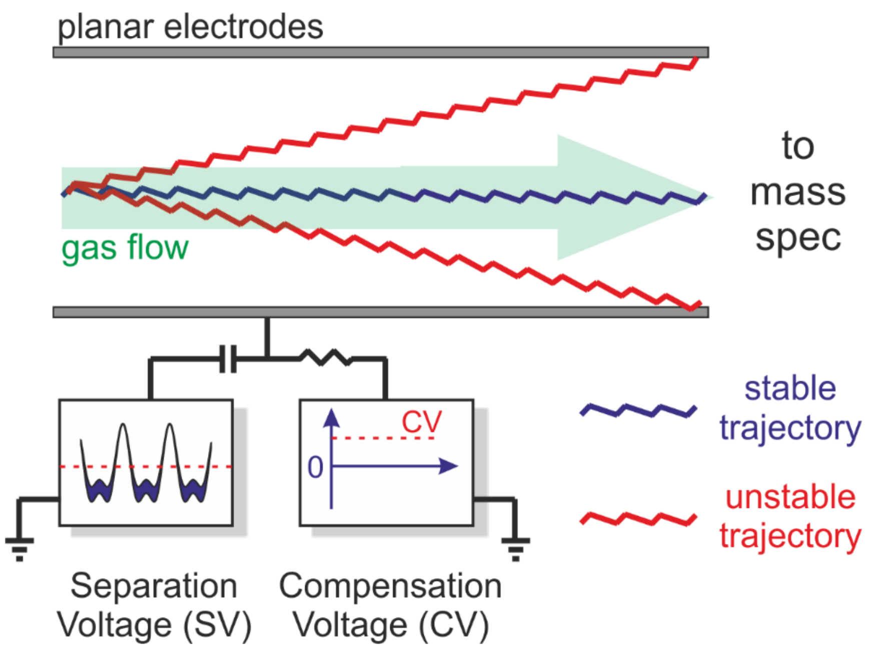
Ion heating



Elongated

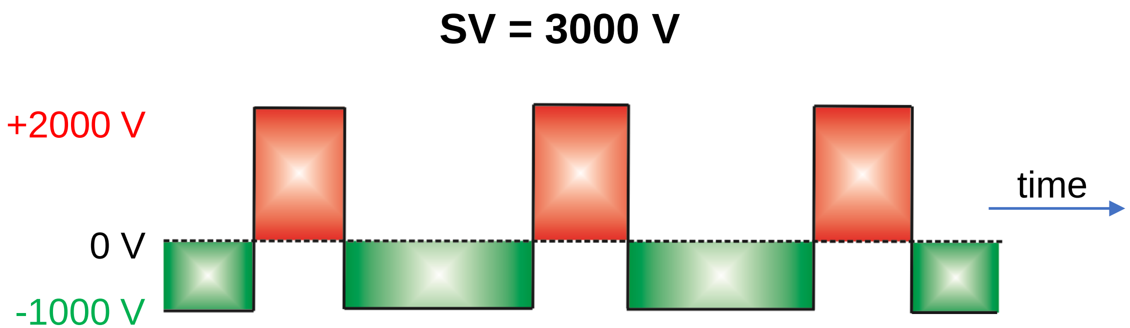
JASMS, 2014, 25, 1384-1393

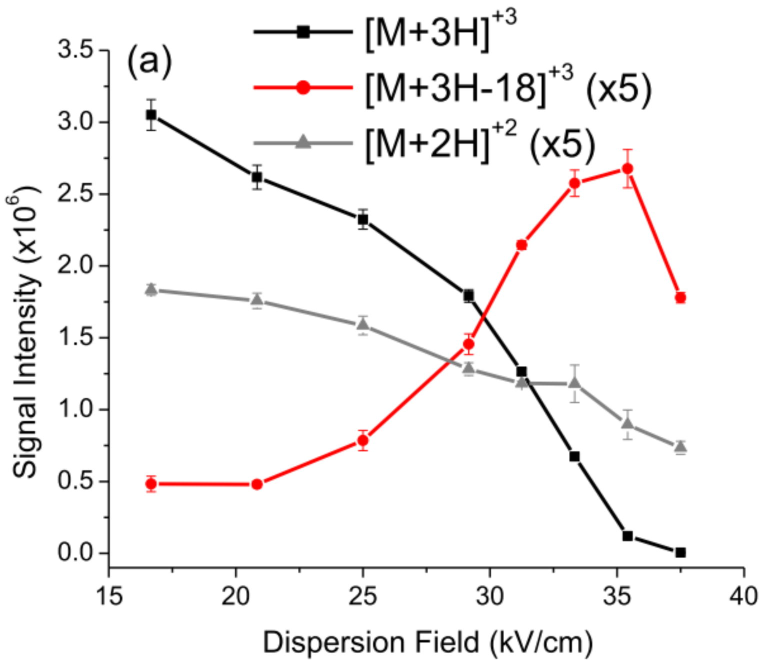
Ion heating and its importance to DMS

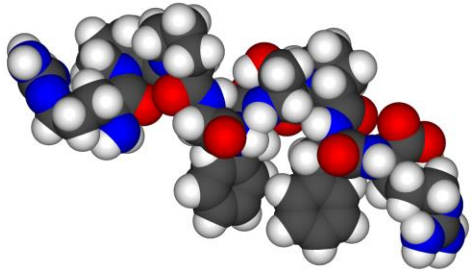


High field strength ($\vec{E}$ =30 – 180 Td) also leads to ion heating, elongation, and fragmentation

SV induced fragmentation of bradykinin







Mol. Phys., 2015, 113, 3151-3158
JASMS, 2017, 28, 2160-2169

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Research Article

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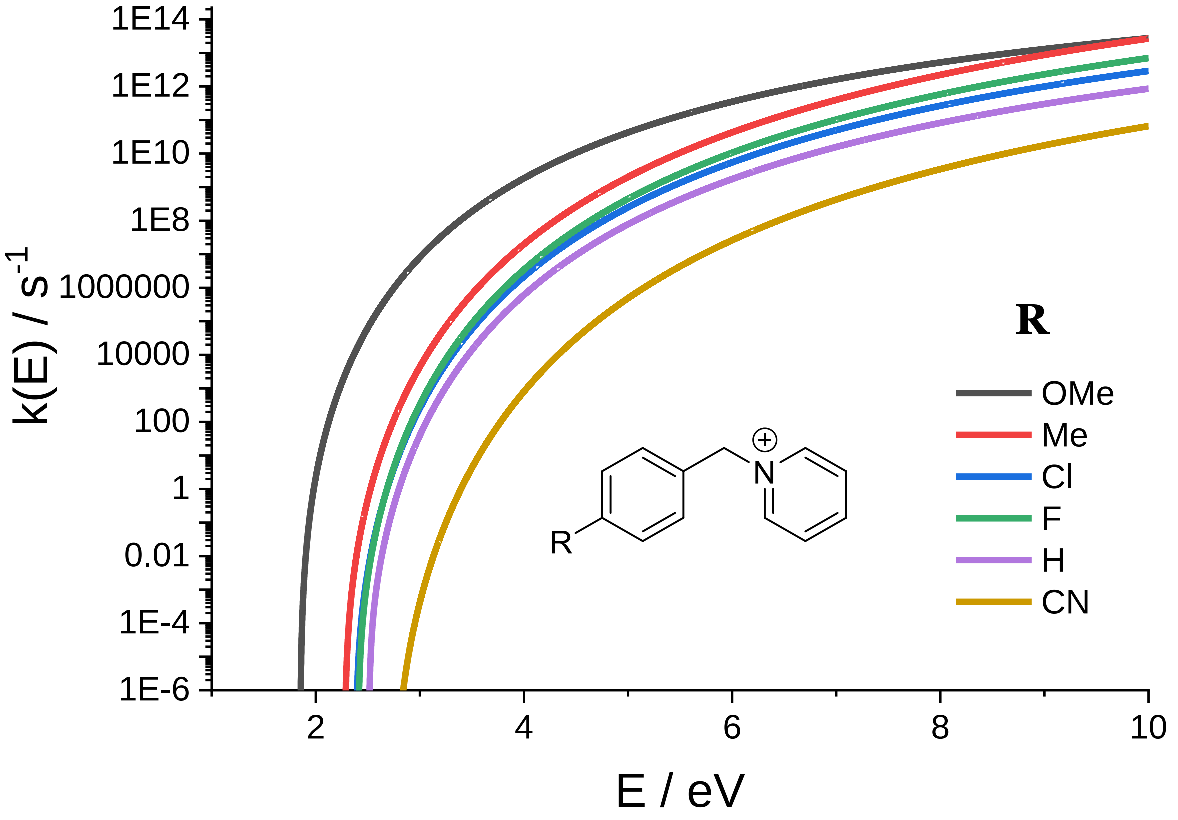
Methods – Modelling dissociation rate

RRKM theory

M⁺ F⁺

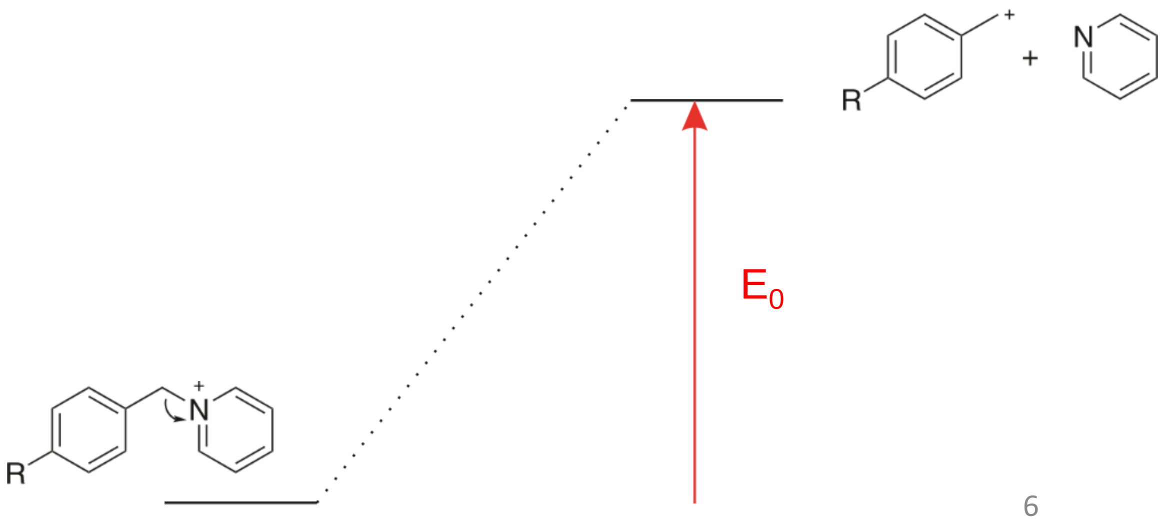


$$k(E) = \frac{G^{\neq}(E - E_0)}{h \cdot N(E)}$$

$G^{\neq}$: sum of rovib states of TS at $E > E_o$

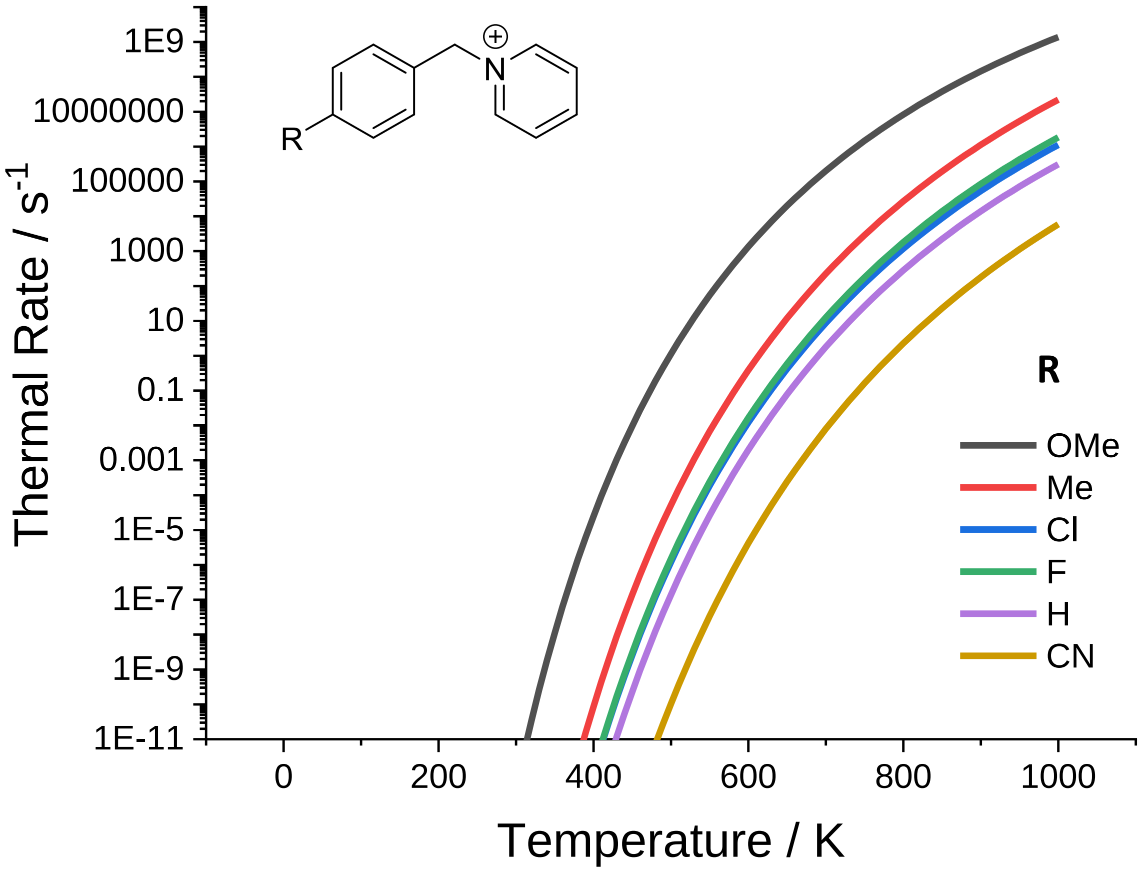
$N(E)$: density of rovib states of GS

TS treated in phase-space limit



Methods – Modelling dissociation rate

Thermal rate k(T)



RRKM rate *k(E)* weighted by a Boltzmann thermal distribution *ρ(E,T)* at temperature *T*

$$k(T) = \int_{E_0}^{\infty} k(E) \cdot \rho(E,T)$$

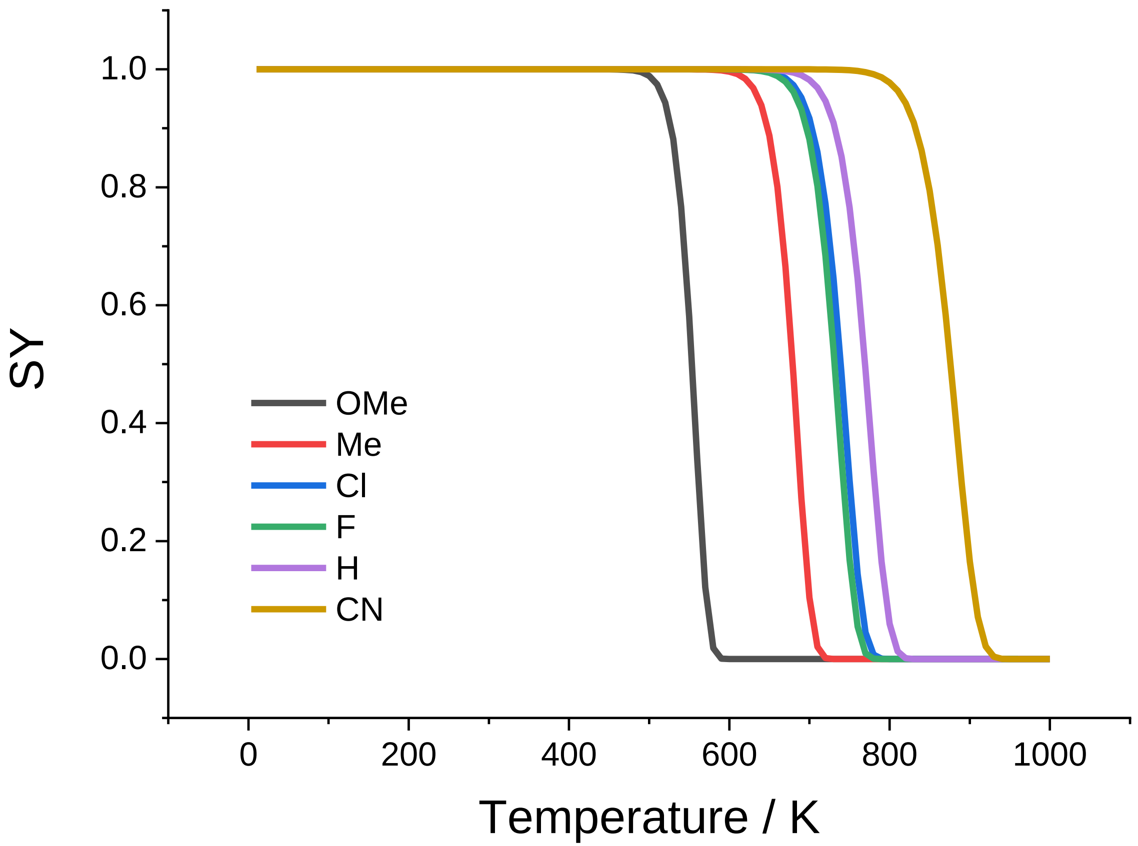
where

$$\rho(E,T) = \frac{\rho(E) \cdot exp(-E/k_b T)}{\int_0^{\infty} \rho(E) \cdot exp(-E/k_b T)\, dE}$$

$$k(T) = \int_{E_0}^{\infty} \frac{G^{\ddagger}(E - E_0)}{h} \cdot \frac{exp(-E/k\,T)}{\int_0^{\infty} \rho(E) \cdot exp(-E/k\,T)\, dE}\, dE$$

Methods – Modelling dissociation rate

Survival Yield (SY)



$$P_d(T) = FY(T) = 1 - exp(-k(T) \cdot \tau) \qquad \tau = \frac{V_{cell}}{Q} = 6.4\ ms$$

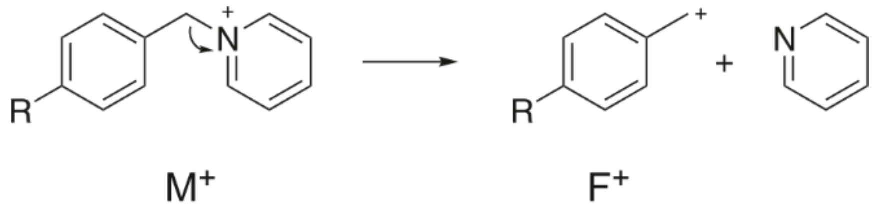
$$SY = 1 - FY$$

Fit SY model to logistic function:

$$SY_{theor} = A_{min} + \frac{(A_{max} - A_{min})}{\left[1 + \left(\frac{x_o}{\boldsymbol{T_{eff}}}\right)^h\right]^s}$$

Experimentally:

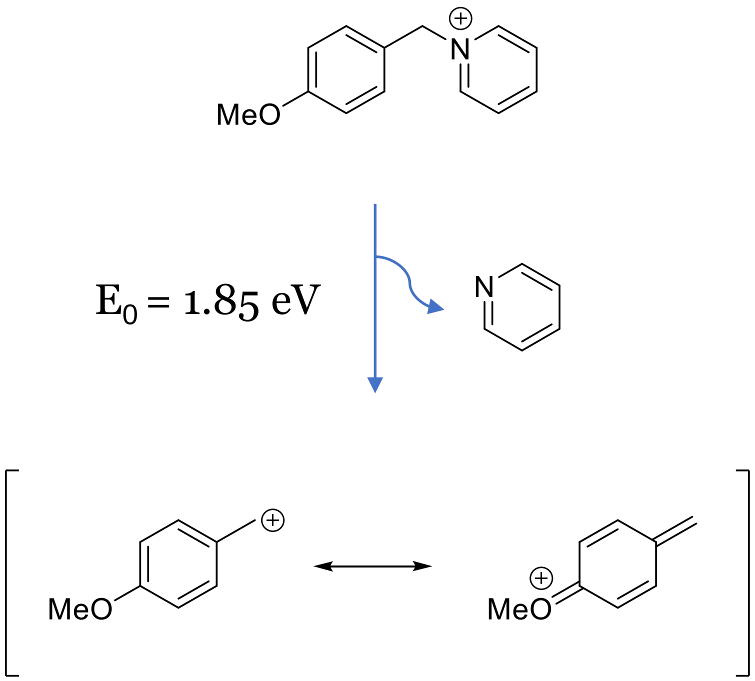
Monitor MRM transitions to get SY with post-DMS potentials minimized



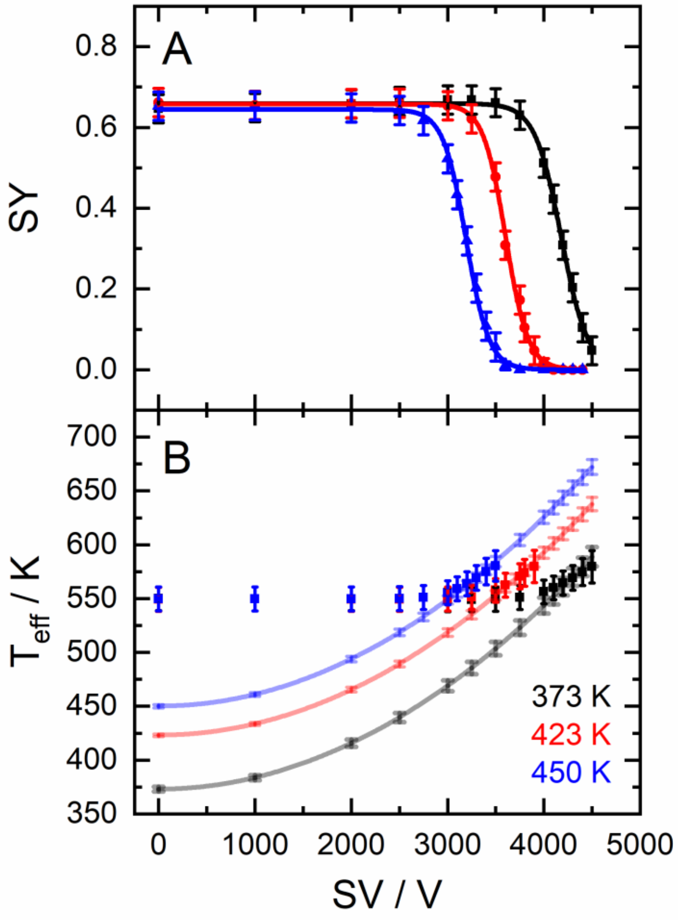
$$FY = \frac{A_{F^+/F^+}}{(A_{M^+/M^+}) + (A_{M^+/F^+}) + (A_{F^+/F^+})} = 1 - SY$$

Determining ion temperatures with thermometer ions

p-methoxy benzylpyridinium (BP) is a robust species for gauging ion temperature



Dissociation observed at all bath gas temperatures



Before onset of dissociation:

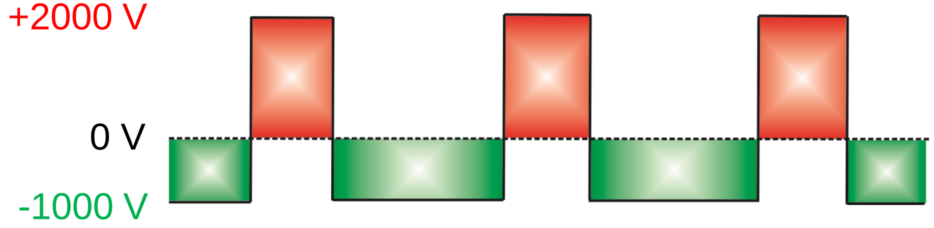
$$T_{eff} = T_{gas} + T_{field}$$

$$T_{eff} \approx T_{gas} + \frac{M}{3k_b}v^2 = \boxed{T_{gas} + \frac{M}{3k_b}(KE)^2}$$

$$\boxed{T_{eff} \approx a + bx^2}$$

Nature of the SV waveform:

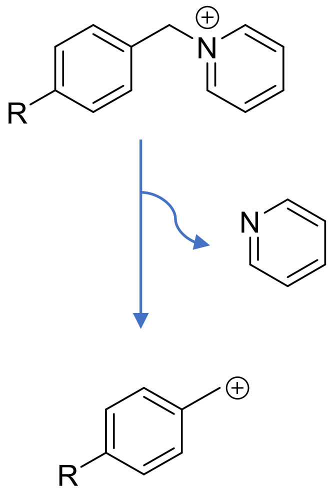
SV = 3000 V



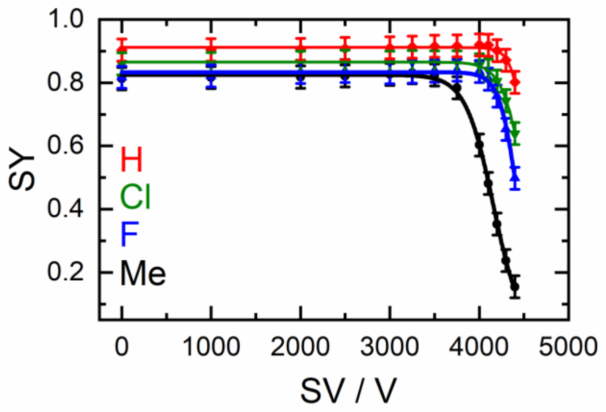
JASMS, 2020, 31, 582-593

Determining ion temperatures with thermometer ions

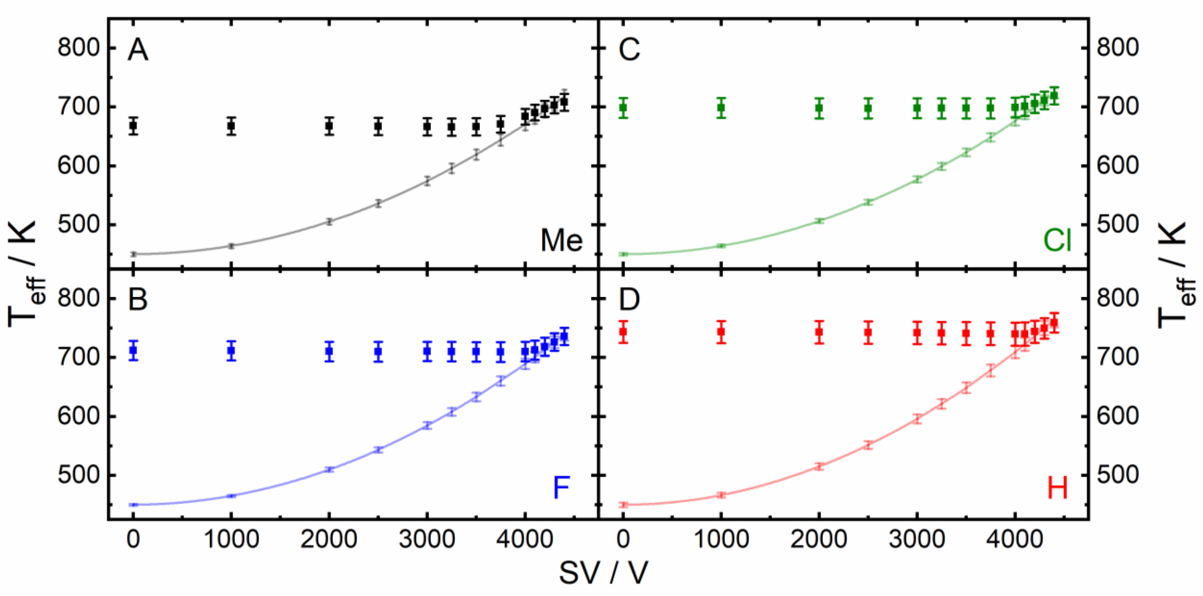
Other benzylpyridinium derivatives can be used, but require high bath gas temperatures to observe dissociation.



T_{bath} = 450 K



T_{bath} = 450 K



R	E_0 / eV	T_{eff} (SV = 4400 V; T_{bath} = 450 K)
OMe	1.85	664 ± 9 K
Me	2.27	708 ± 14 K
F	2.39	736 ± 15 K
Cl	2.37	719 ± 15 K
H	2.50	759 ± 17 K

The degree of ion heating imparted is related to the density of states of the BP ion

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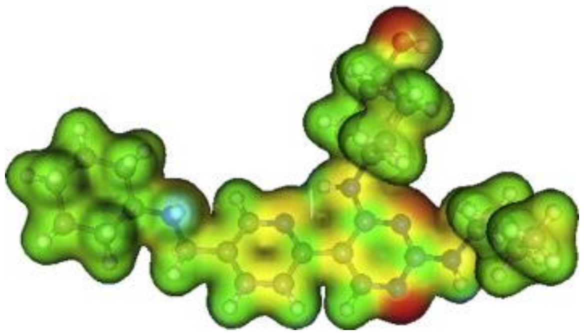
Dependence of T_{eff} on ion structure

Collision frequency (collision cross section)



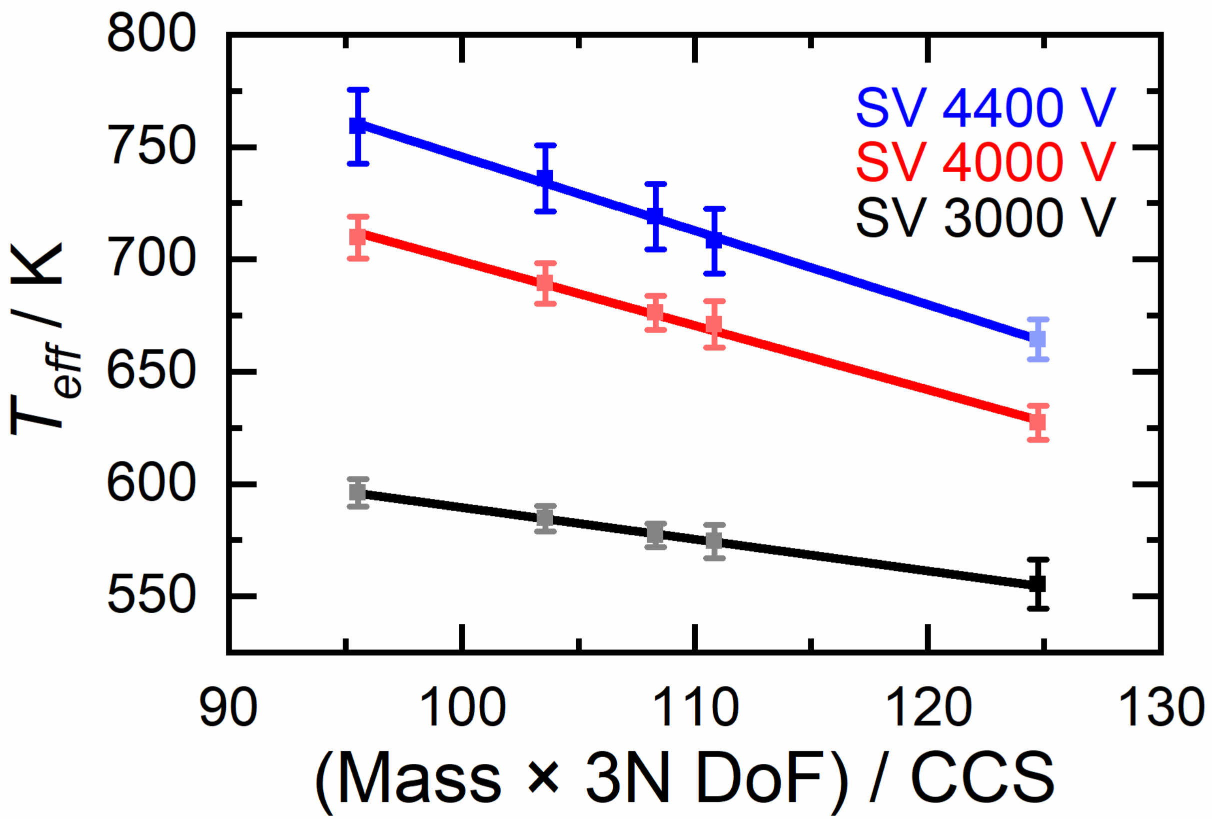
Density of states (mass-weighted degrees of freedom)

4-fluoro BP

Ω_{N2} = 136 Å^2
75 DoF
188.1 Da
T_{eff} = 736 K (4400 SV)

4-chloro BP

Ω_{N2} = 141 Å^2
75 DoF
204.1 Da
T_{eff} = 719 K (4400 SV)



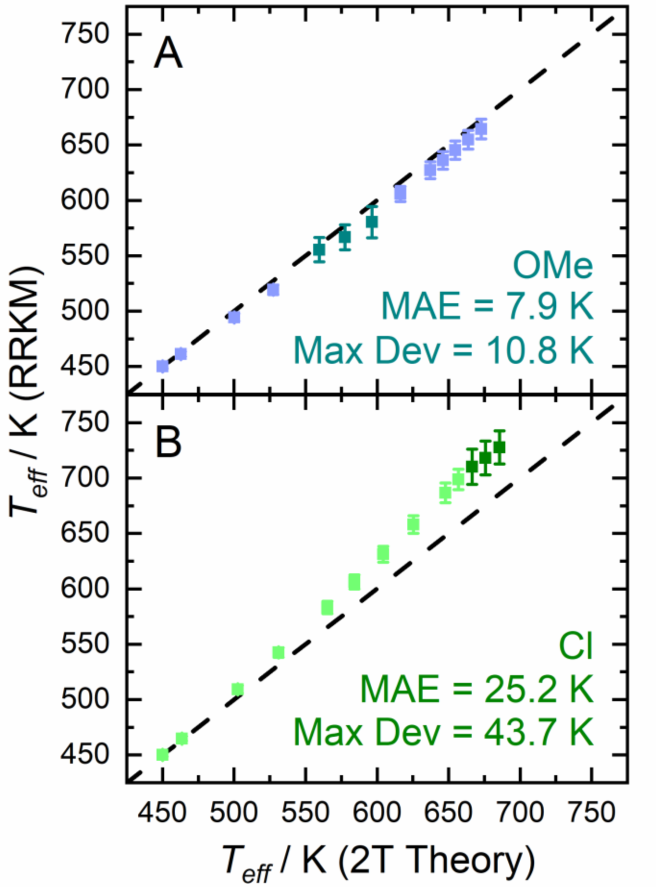
Two temperature theory predictions of T_{eff}

Self-consistent evaluation approach ($\Delta T_{eff} < 10^{-4}$ K) :

$$K = \frac{\sqrt{18\pi}}{16}\sqrt{\frac{1}{m_{ion}} + \frac{1}{m_{gas}}}\,\frac{ze}{\sqrt{k_b T_{eff}}}\,\frac{1}{\Omega_{N_2}(T_{eff})\cdot N}$$

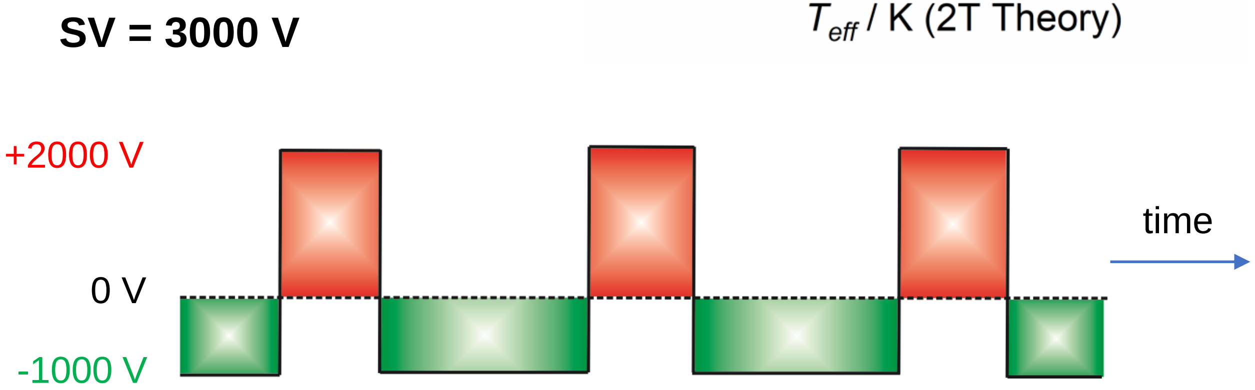
$$T_{eff} = T_{gas} + T_{field} \approx T_{gas} + \frac{M}{3k_b}(KE)^2$$

2T theory suggests ion heating is governed by the amplitude of the high-field portion of the SV waveform



Limitations of self-consistent 2T theory method:

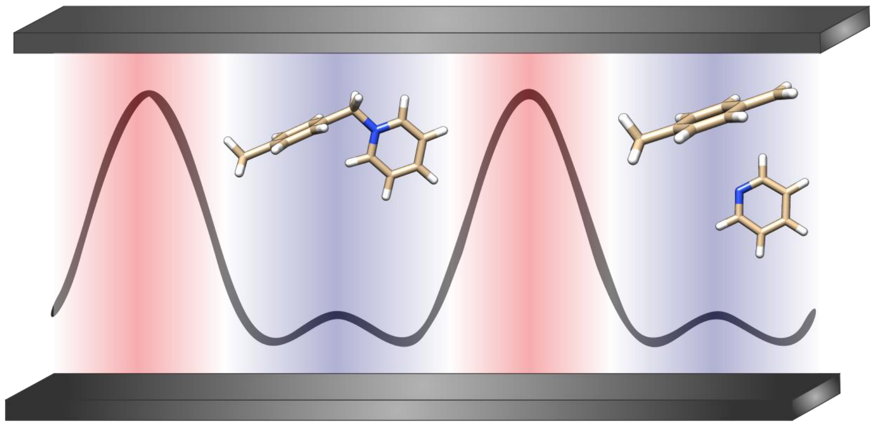
1. Field dependency of ion mobility K ($\vec{E}$>> 30 Td)
2. Neglecting instantaneous ion velocities ($v \leq KE$)
3. The possibility of ion heating during the low-field portion of the waveform at high SV



Concluding remarks and applications

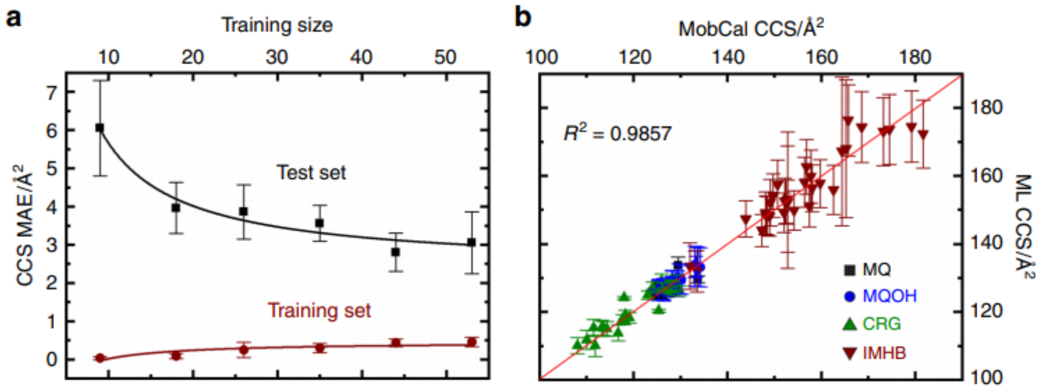
Summary:

1. Ion temperatures reach a maximum of 759 K on the SCIEX SelexION system
2. Ion heating correlates linearly with ion structure
3. 2T theory yields good estimates of ion temperature using the self-consistent approach

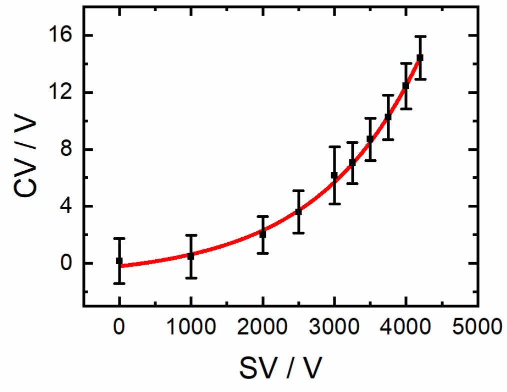


Applications:

ML prediction of physicochemical properties

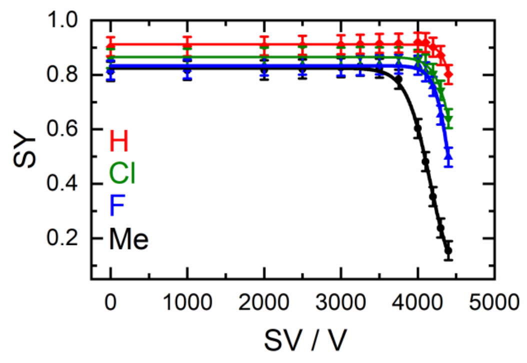


BP ions as calibrants of SV field



SV/CV pairs

+



Monitoring SY

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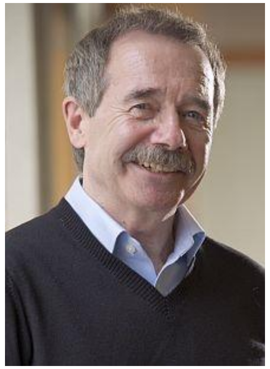
Nat. Comm., 2018, 9, 5096

Acknowledgements

PhD Advisory Committee

Prof. W. Scott Hopkins



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Collaborators, Resources, and Funding

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