

Ion Mobility Spectrometry Determination of Rates of Decomposition of Ions of Explosives: The Build and the Qualification 2008-9



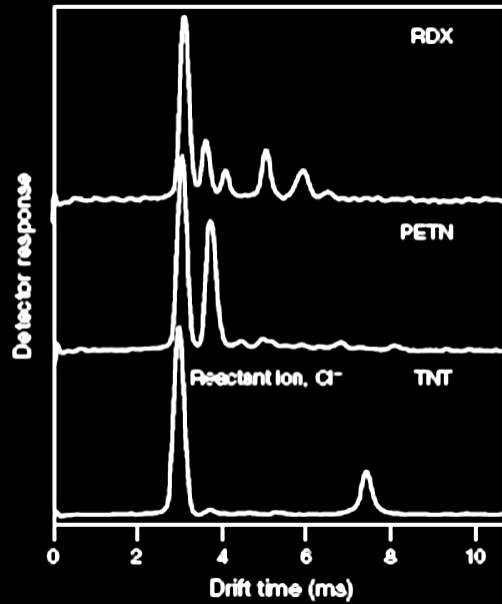
**NM
STATE**

G.A. Eiceman, X. An, J.A. Stone¹
Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces, NM
¹Department of Chemistry, Queens University, Kingston, Ontario Canada

CRITICAL TECHNOLOGY



.....AND RESPONSIBLE KNOWLEDGE

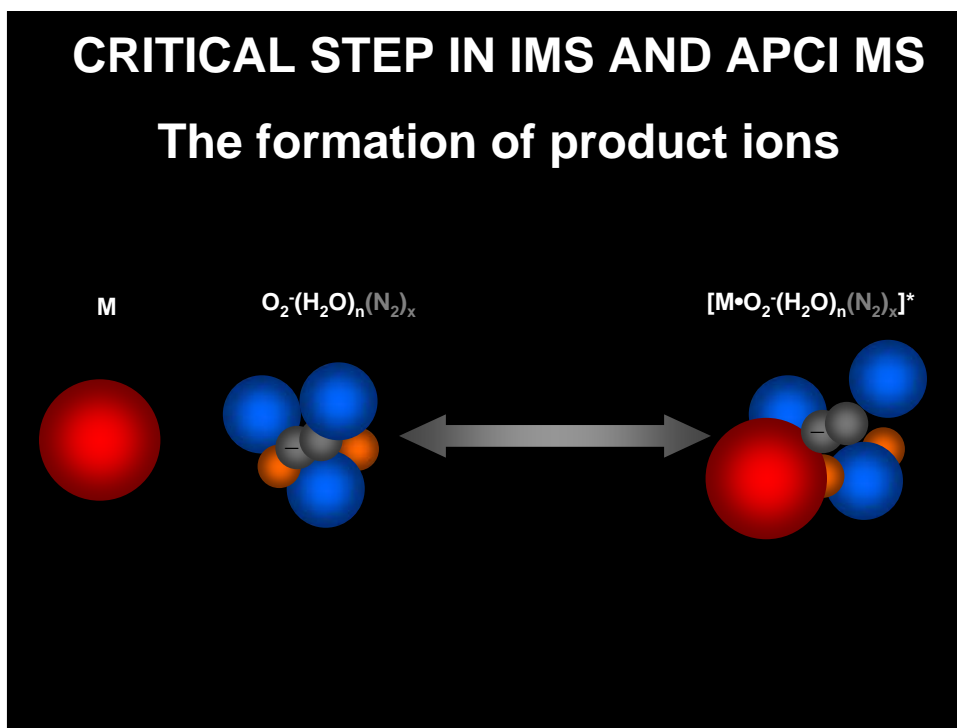


PROPERTIES OF EXPLOSIVES

Molecular Weight	✓
Melting Point	✓
Vapor Pressure	✓
Decomposition Temperature	✓
Thermal ignition temperature	✓
Crystal density	✓
Energy of formation	✓
Enthalpy of formation	✓
Detonation Velocity	✓
Strength and Brisance values	✓
On gas ions	nothing

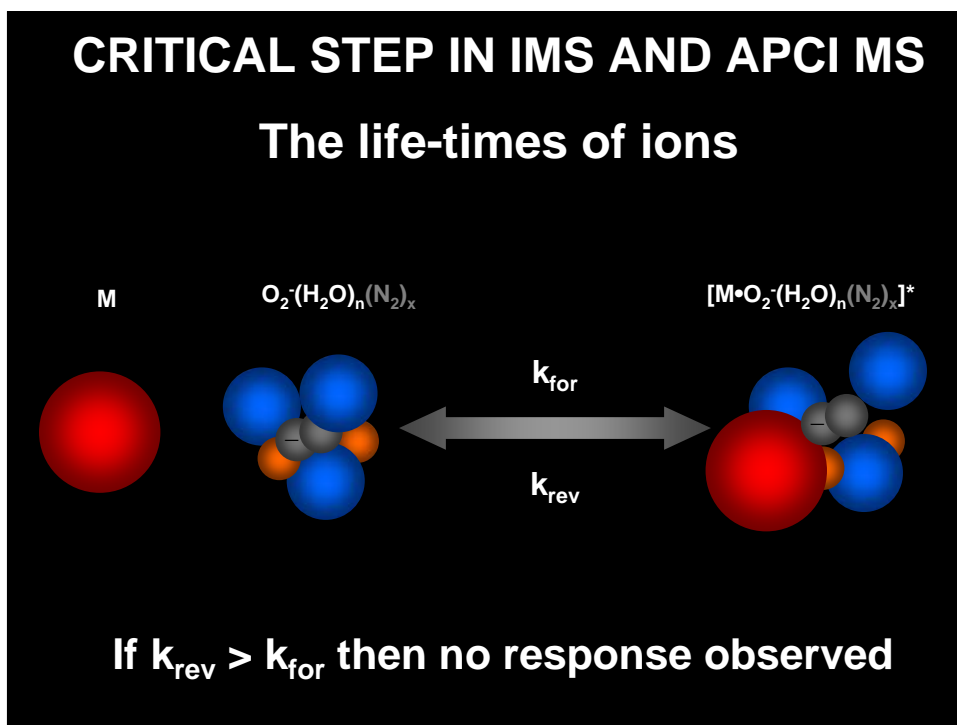
CRITICAL STEP IN IMS AND APCI MS

The formation of product ions

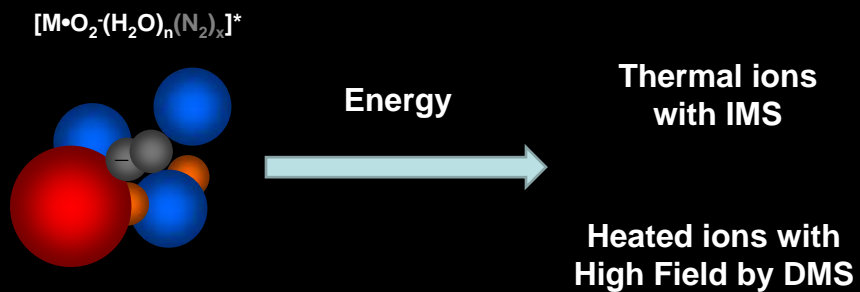


CRITICAL STEP IN IMS AND APCI MS

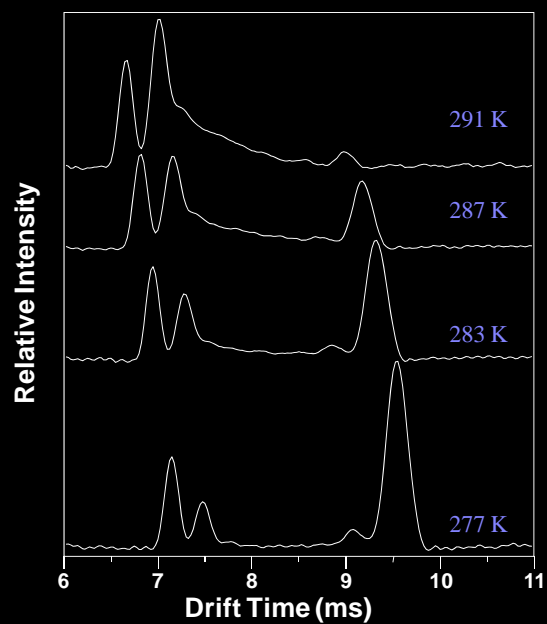
The life-times of ions



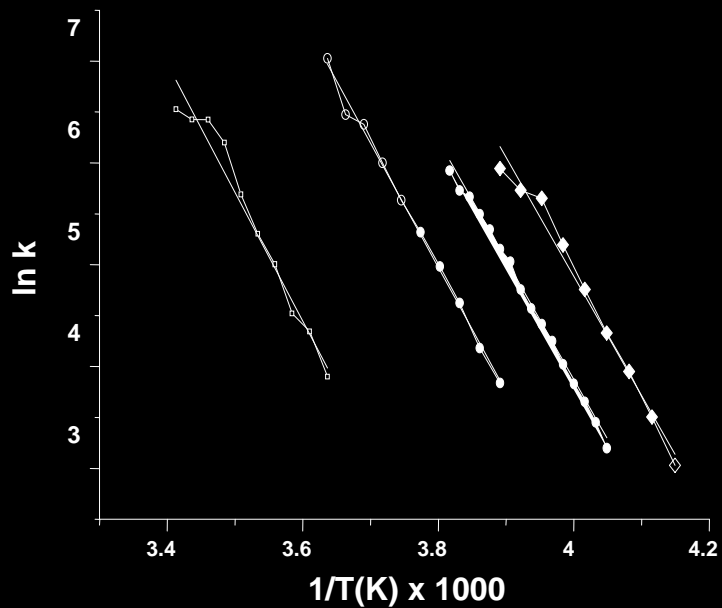
HOW TO MEASURE ION LIFETIMES BY OBSERVING DEPENDENCE ON HEAT OR ENERGY



ION KINETICS BY IMS

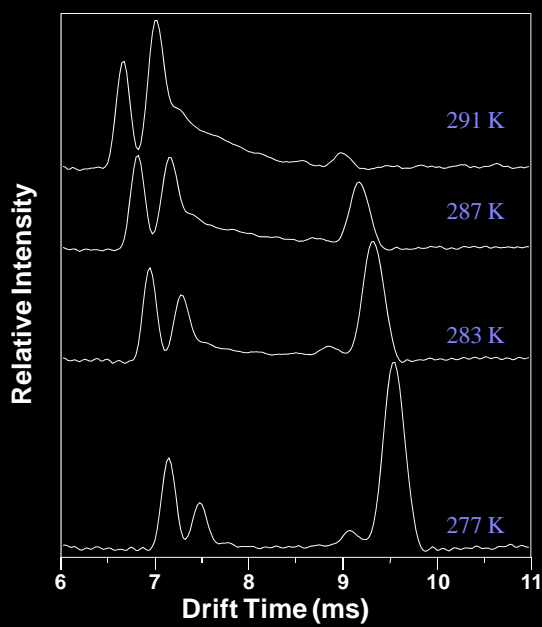


HEAT OF DISSOCIATION OF PBD

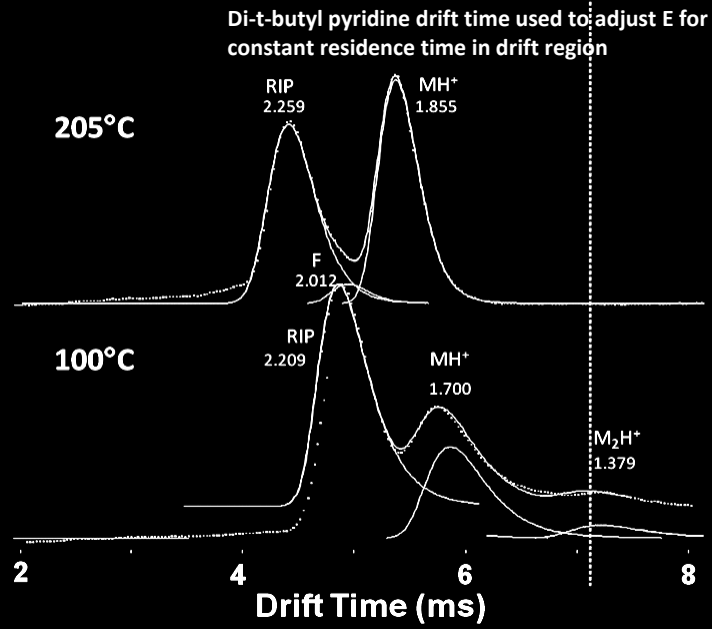


The kinetics of the decompositions of the proton bound dimers of
1,4-dimethylpyridine and dimethyl methylphosphonate from
atmospheric pressure ion mobility spectra

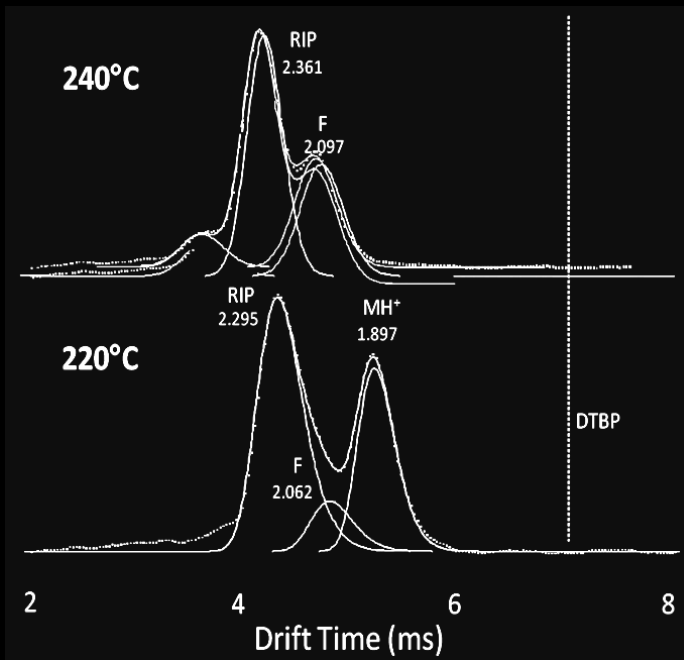
R.G. Ewing^{a,*}, G.A. Eiceman^b, C.S. Harden^c, J.A. Stone^d

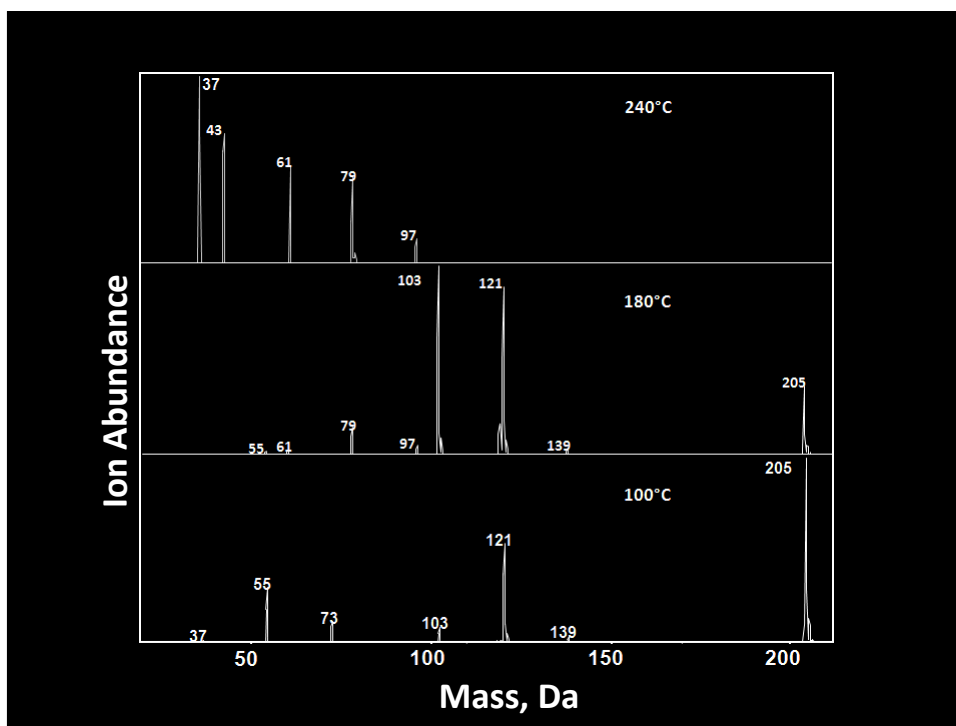


**PROPYL ACETATE IN AT
300 V/cm and const
residence time**

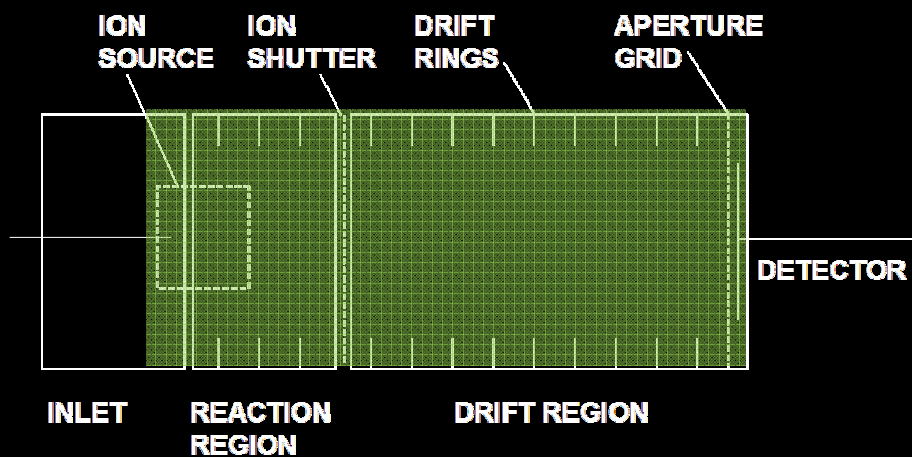


**PROPYL ACETATE IN AT
300 V/cm and const
residence time**

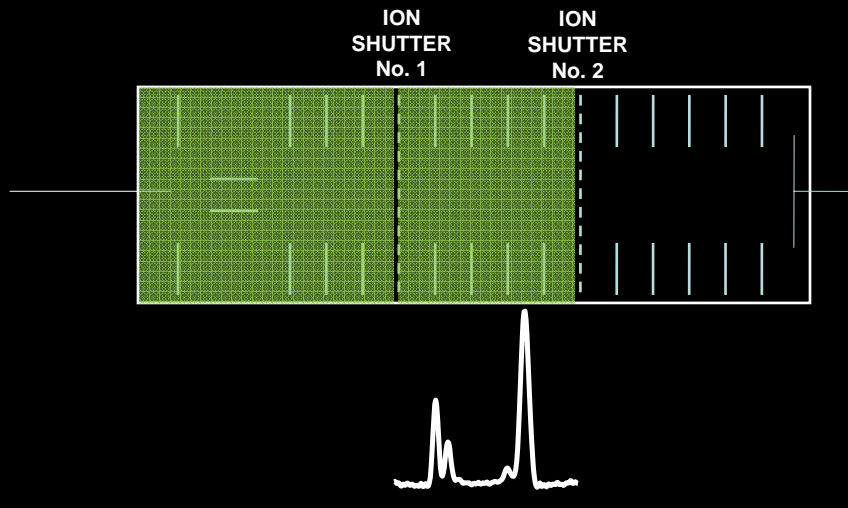




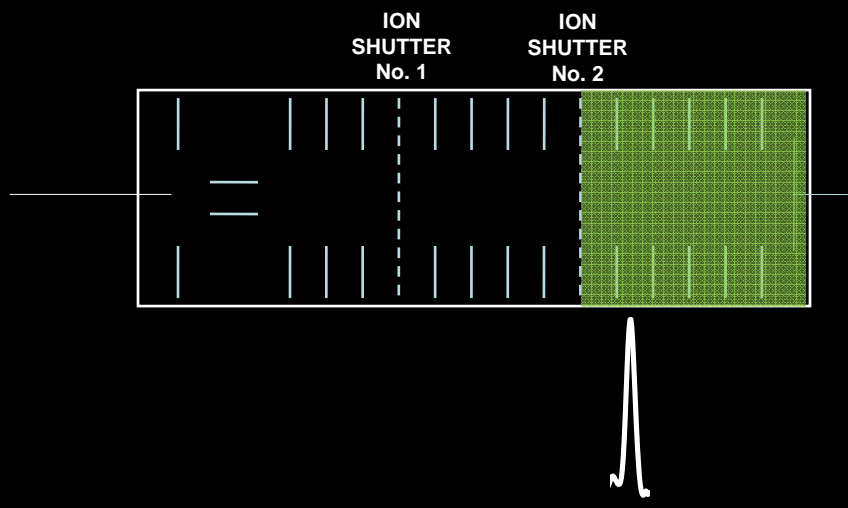
**CANNOT QUANTITATIVELY
ASSIGN ION INTENSITY DUE TO
SOURCE-DRIFT CONNECTION**



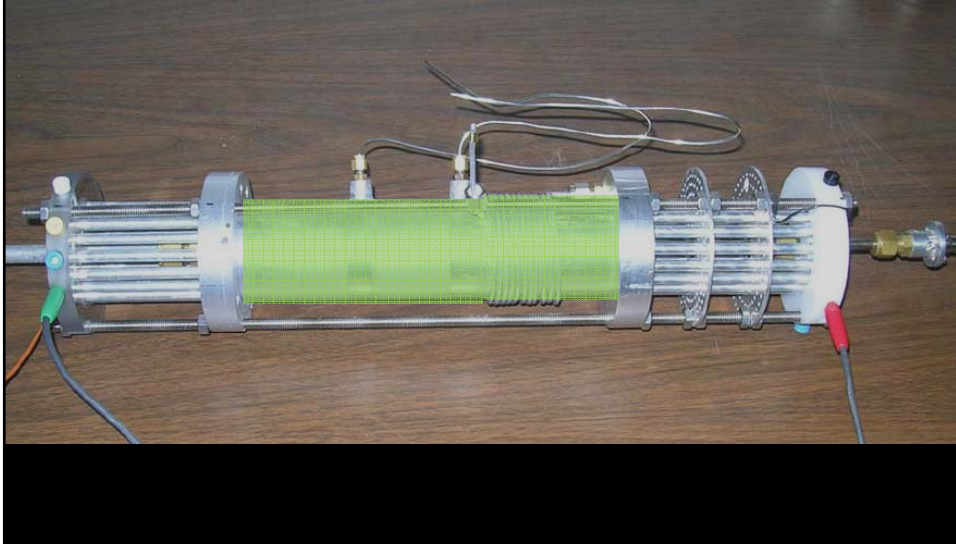
SOLUTION: ISOLATE SOURCE FROM DRIFT REGION BY ION SELECTION



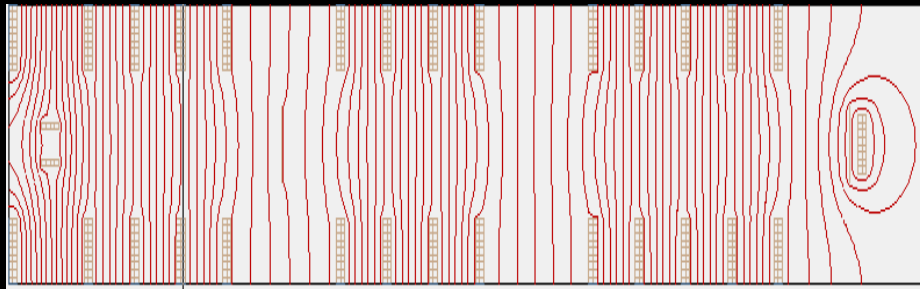
SOLUTION: ISOLATE SOURCE FROM DRIFT REGION BY ION SELECTION



NMSU KINETIC IMS

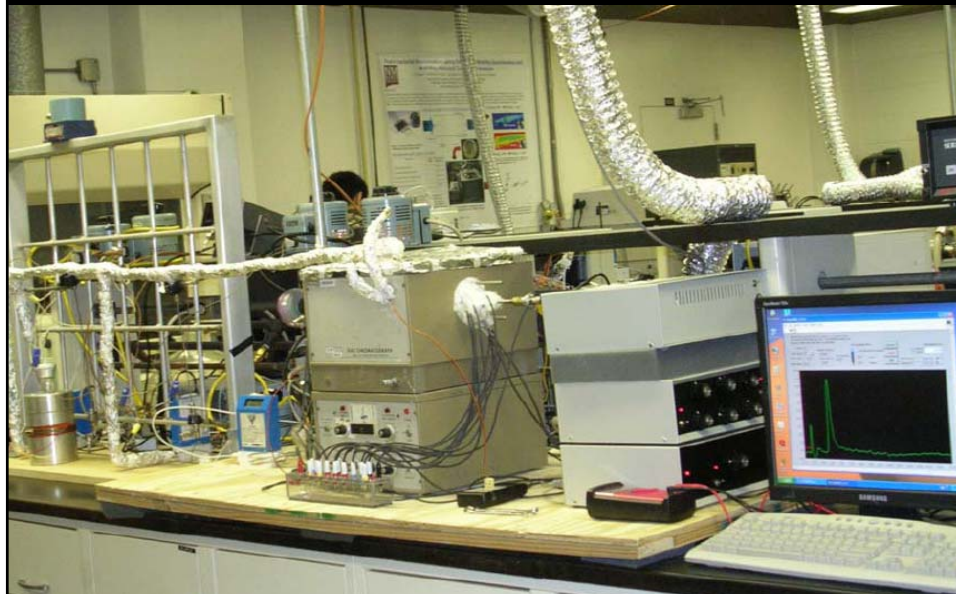


NMSU KINETIC IMS

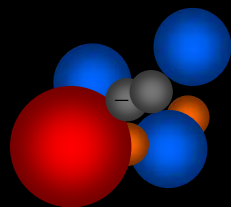
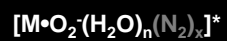


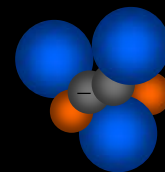
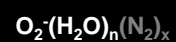
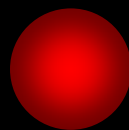
Simion simulation of the IMS

NMSU KINETIC IMS



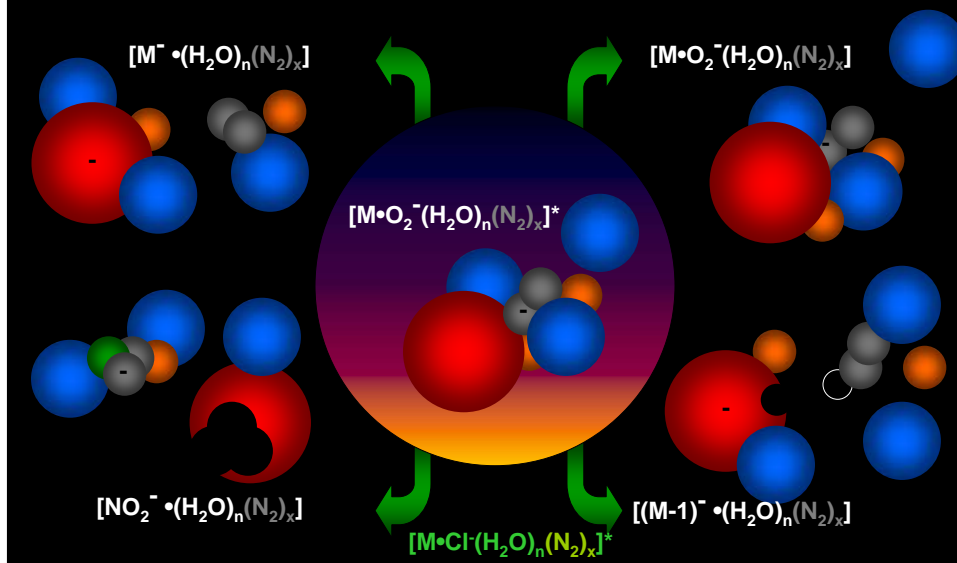
CRITICAL STEP IN IMS AND APCI MS


$$k_{rev}$$

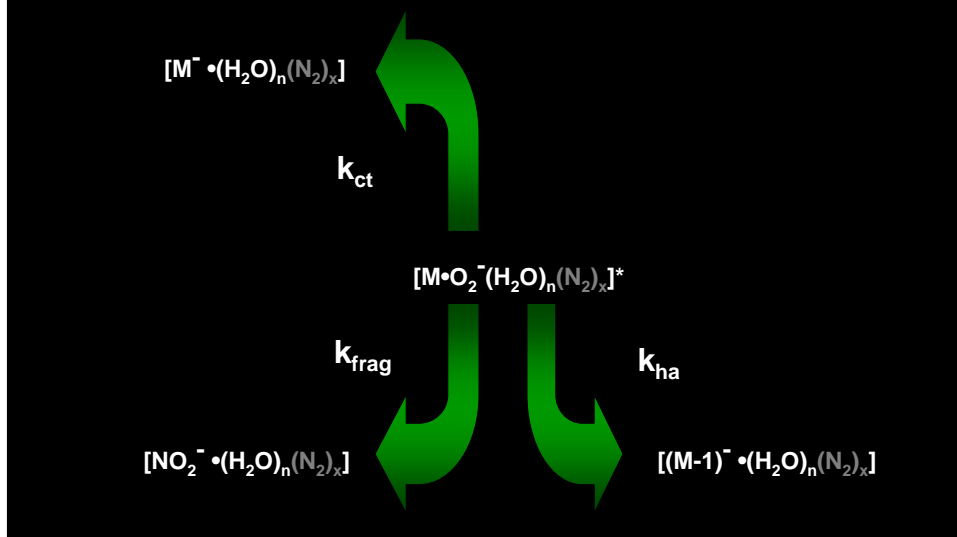
$$M$$


CHEMISTRY OF EXPLOSIVES

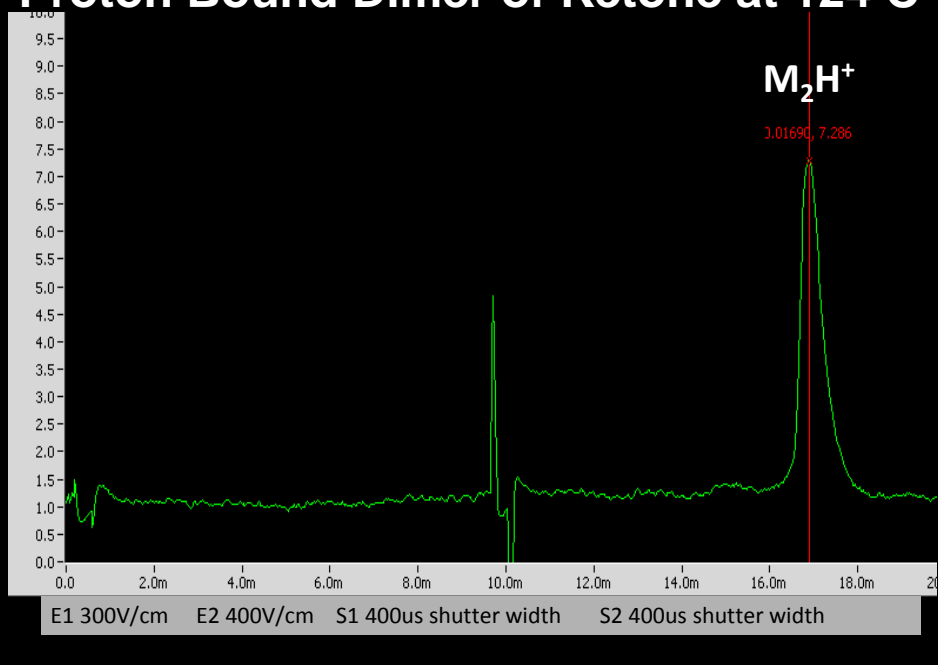
R.E. Ewing, G.J. Ewing, D.A. Atkinson, and G.A. Eiceman, Talanta, 2001, 54, 515-529.



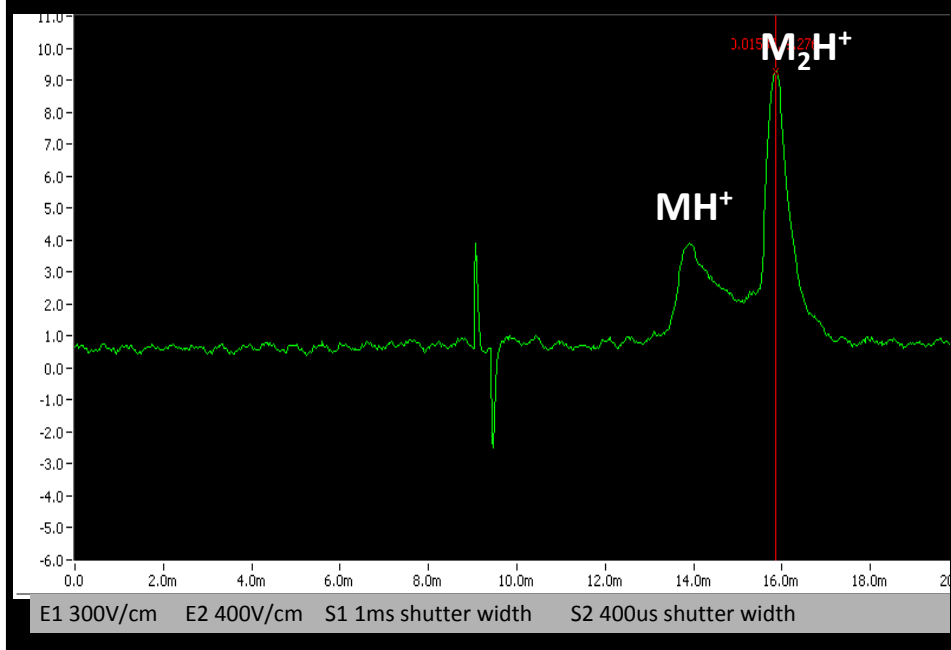
MISSING IN DATA BASES ON EXPLOSIVES

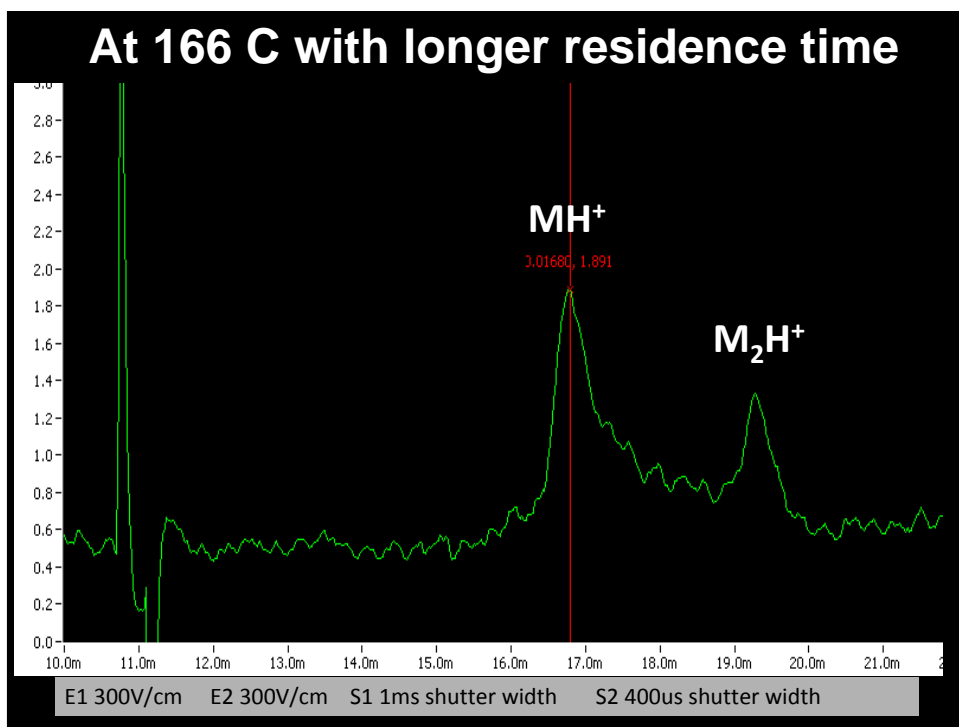
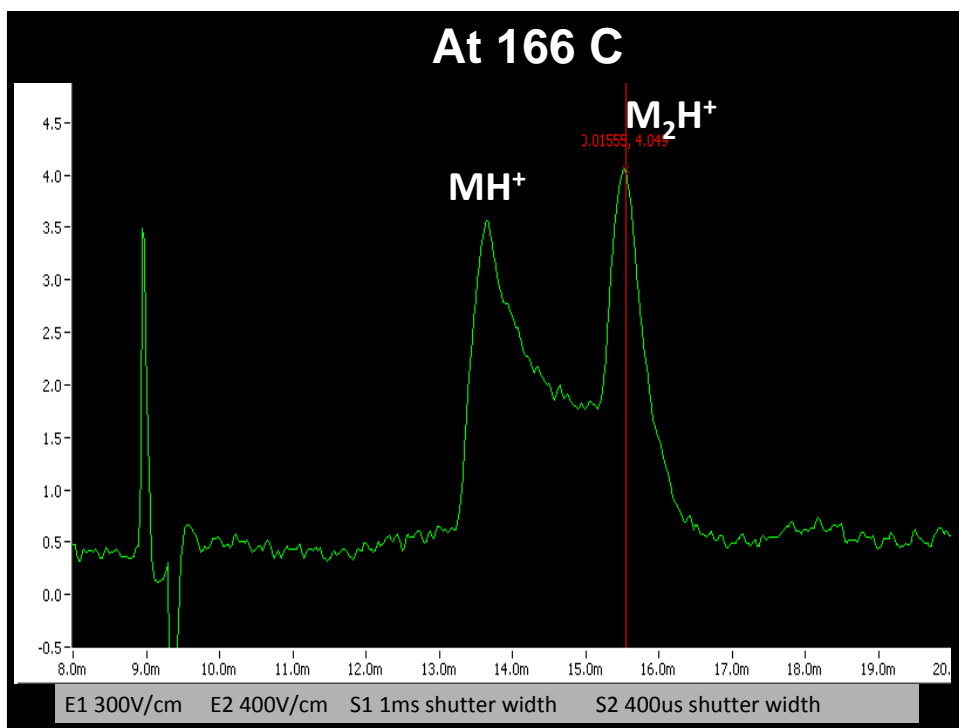


Proton Bound Dimer of Ketone at 124 C

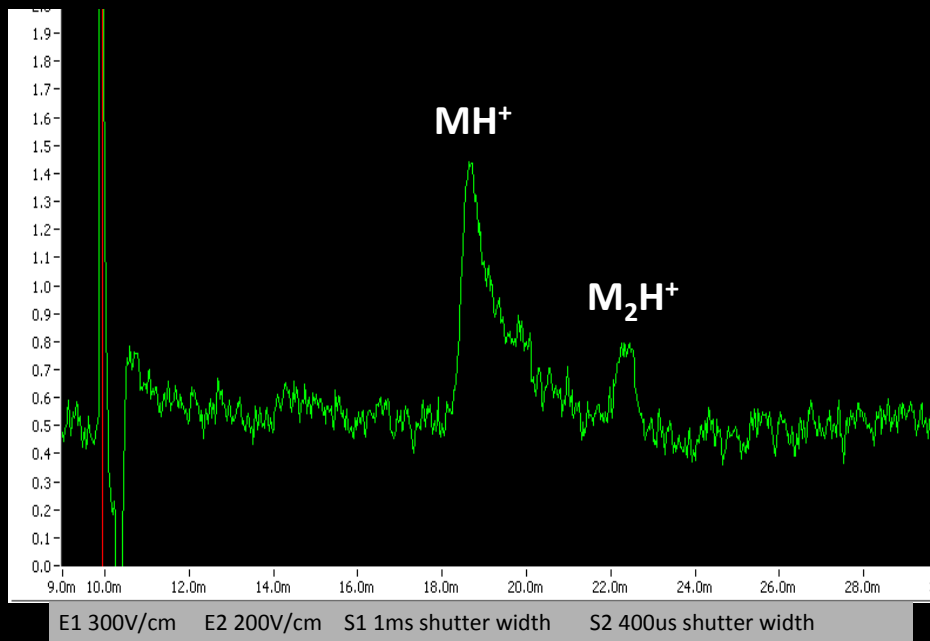


At 150 C

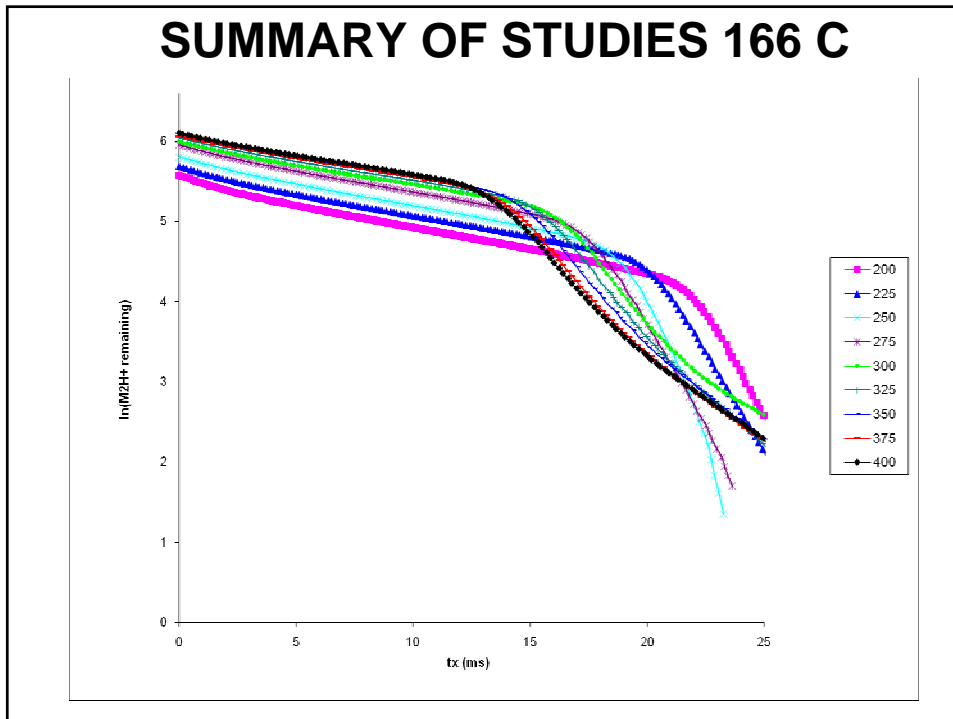




At 166 C still longer residence time

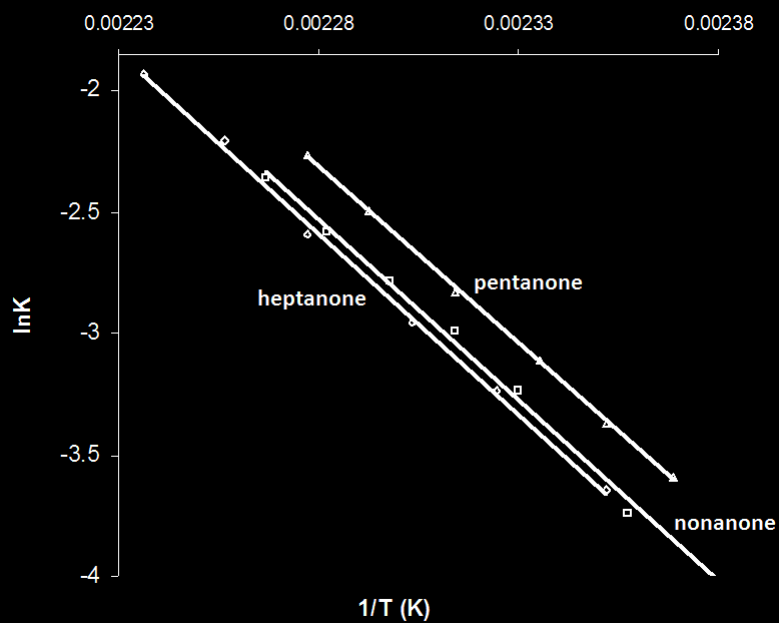


SUMMARY OF STUDIES 166 C



RATES AT 161 C

field (V/cm)	k $10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
175	0.05158
200	0.05307
225	0.05260
250	0.05371
275	0.05181
300	0.04918
325	0.04944
350	0.05000
375	0.04968
400	0.04917
avg_k	0.05102
sd	0.00173
%RSD	3.396



VALIDATION OF KINETIC IMS

pentanone. The enthalpy changes from NIST for the association reaction are -121, -131 and -126 kJ/mol. The first and last are by T. McMahon and the other by M. Meot-Ner. The associated entropy changes are, respectively, -149, -141 and -131 J/(K mol). We obtain 120.6 kJ/mol for E_a , which can be equated to ΔU° , as ($H = U + PV$) in

$$\Delta H^\circ = \Delta U^\circ + \Delta(PV) = E_a + \Delta(nRT) = E_a + (\Delta n)RT.$$

For the dissociation $M_2H^+ \rightarrow MH^+ + M$, $\Delta n = 2 - 1 = +1$. Then, taking 158 C, the midpoint of our temperature range, $(\Delta n)RT = 1 \times 8.314 \times 431 = 3.6$ kJ/mol. Hence, for the dissociation reaction, $\Delta H^\circ = 124.2$ kJ/mol.

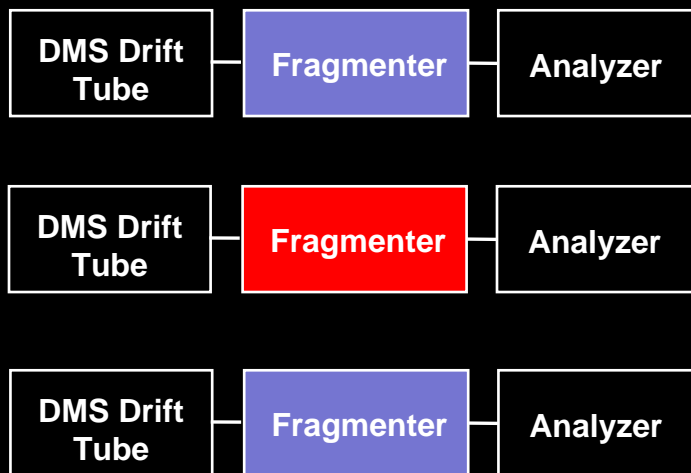
This is right in the middle of the literature values,

CONCLUSIONS ON IMS

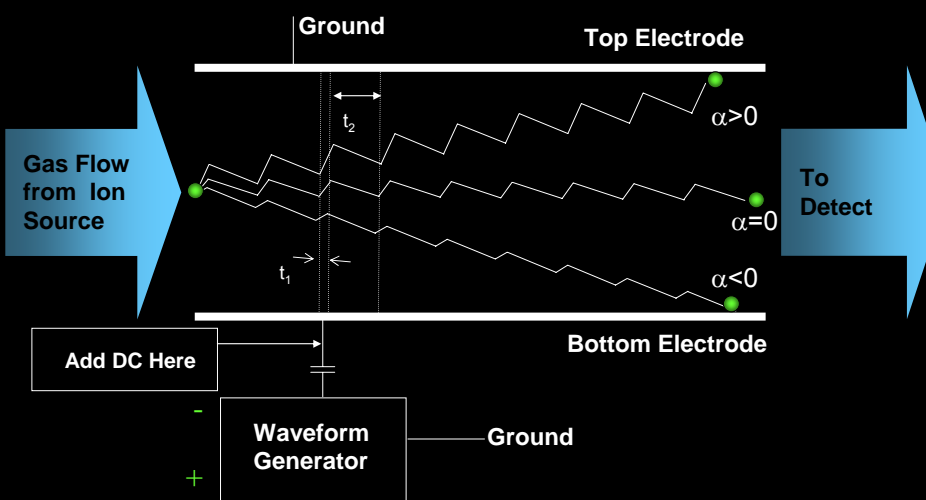
1. Plot $\ln k$ versus $1/T$ to obtain H and S
2. Kinetics first proven with Ketones matches literature by another method
3. DATA GOOD...ON TO EXPLOSIVES



ANOTHER CONCEPT FOR REDUCED FALSE ALARMS IN IMS OR MS



ION DECOMPOSITION BY 1 MHz ELECTRIC FIELD

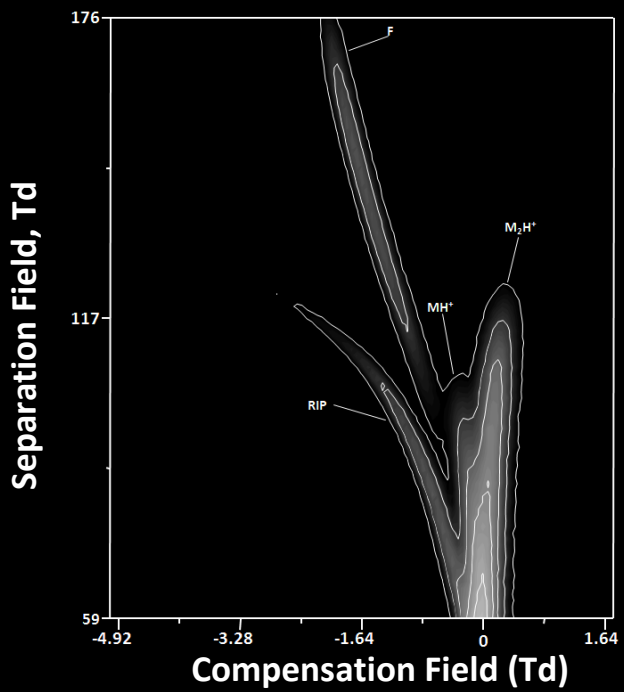


STUDIES MADE WITH SIONEX SVAC AND NMSU DMS/MS



SIONEX Corporation www.sionex.com

ELECTRIC FIELD HEATING PROPYL ACETATE AT 100°C

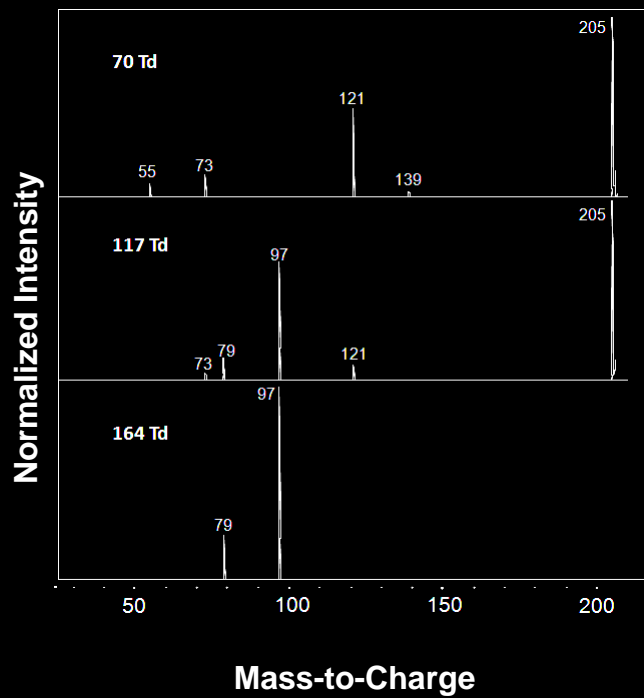


Fragmentation pathways and mechanisms of aromatic compounds in atmospheric pressure studied by GC-DMS and DMS-MS. International Journal of Mass Spectrometry 2007, 263, (2-3), 137-147.

Shai Kendler, Gordon R. Lambertus, Barry D. Dunietz, Stephen L. Coy, Erkinjon G. Nazarov, Raanan A. Miller and Richard D. Sacks

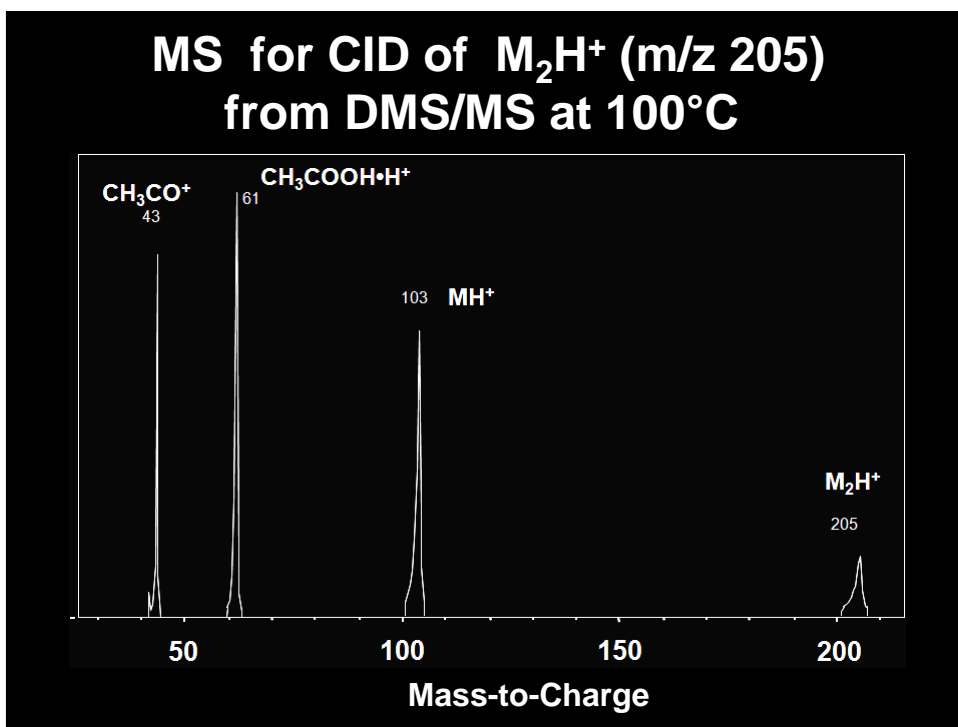
DMS-pre-filtered time-of-flight mass spectrometry (DMS-MS) has been used to verify the chemical composition of the ion species resolved by GC-DMS. This work focuses on the fragmentation of diaryl compounds, including diphenyl methane (DPM) and bibenzyl (BB), using information from the DMS and DMS-MS spectra of a series of aromatic compounds..... DPM-H⁺ is observed to undergo field-induced fragmentation in the DMS to produce C₇H₇⁺(Bz⁺) and unobserved neutral benzene with a low energy barrier. In contrast, BB-H⁺ fragments to C₈H₉⁺ and benzene with a higher energy barrier. Calculated barriers and experimental results are in qualitative agreement. It is suggested that CID in DMS can further enhance DMS analytical performance

**MASS SPECTRA FROM DMS
MS OF PROPYL ACETATE
AT 100°C**

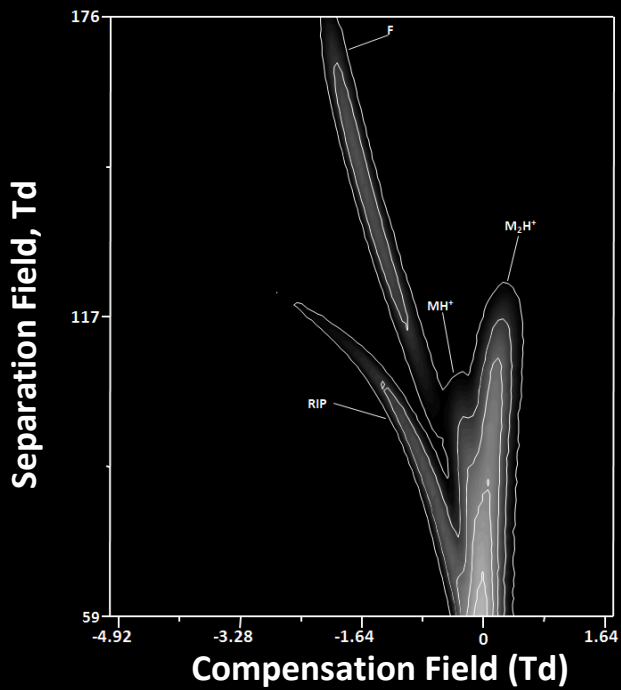


MASS ASSIGNMENT OF DMS MS OF PROPYL ACETATE AT 100°C

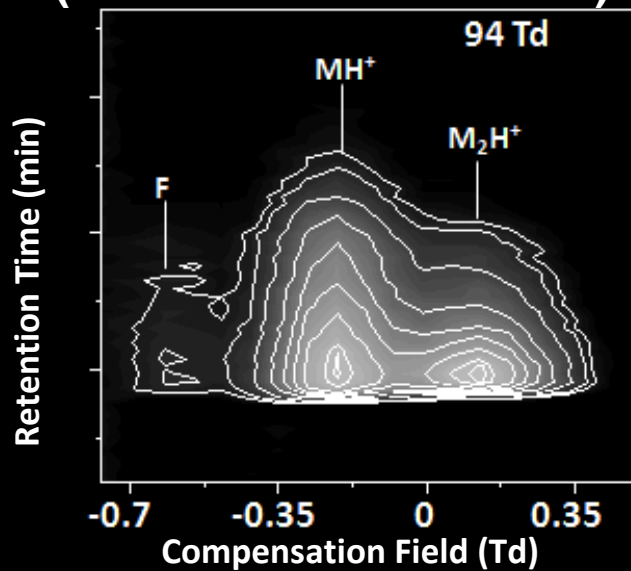
ion	mass Da				
	M_2H^+	205			
$MH^+(H_2O)_n$	103	121	139	n	
	0	1	2		
$CH_3COOH \cdot H^+(H_2O)_n$	61	79	97	115	n
	0	1	2	3	
CH_3CO^+	43				



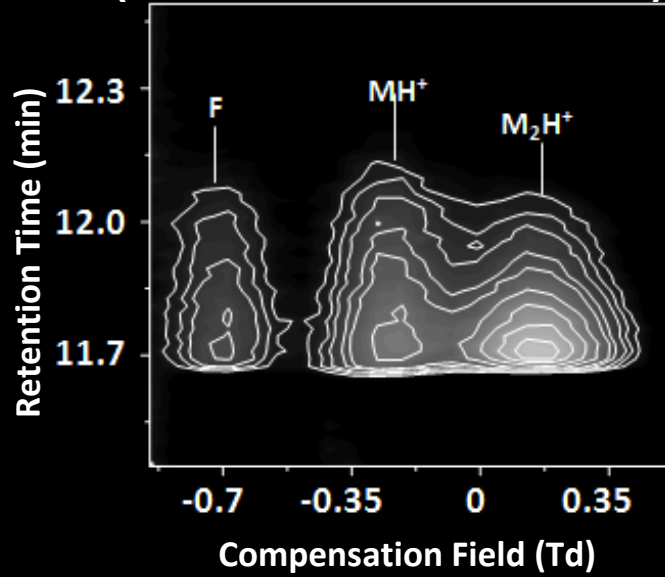
**ELECTRIC FIELD HEATING
PROPYL ACETATE AT 100°C**



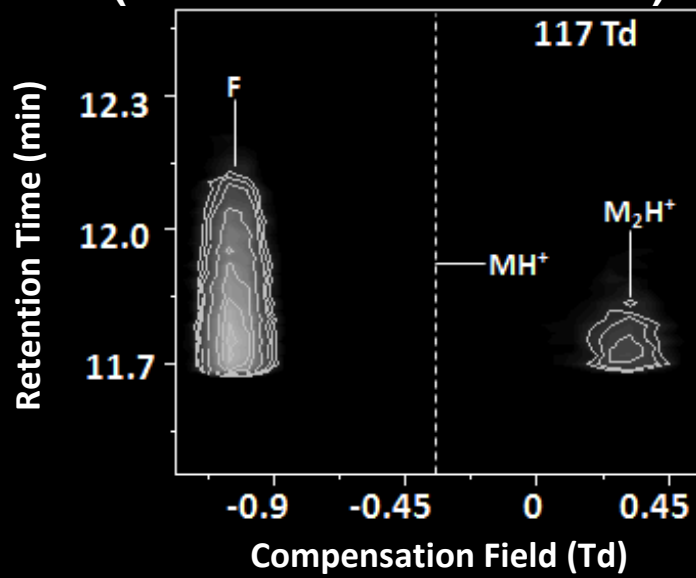
**GC DMS STUDIES
(AVOIDING IMPURITIES)**



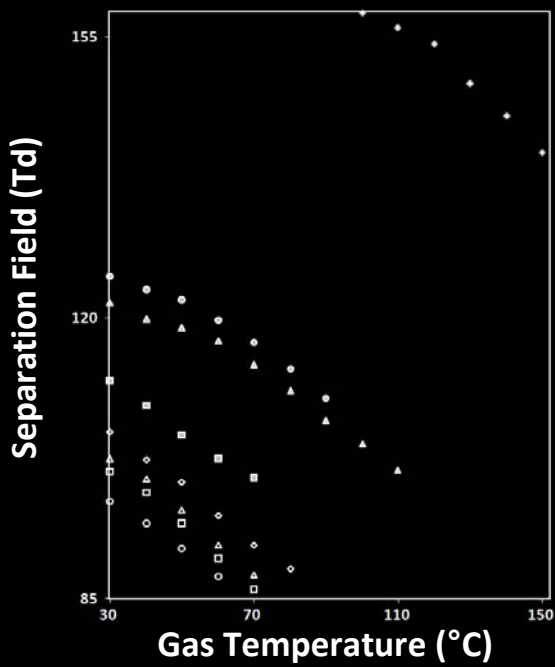
GC DMS STUDIES (AVOIDING IMPURITIES)



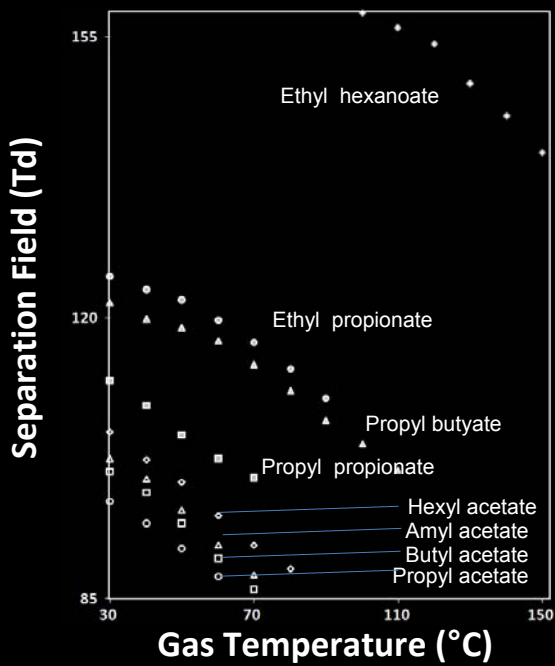
GC DMS STUDIES (AVOIDING IMPURITIES)



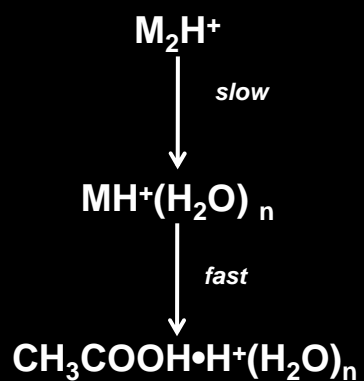
APPEARANCE FIELD FOR FRAGMENT IONS WITH Td AND GAS TEMPERATURE



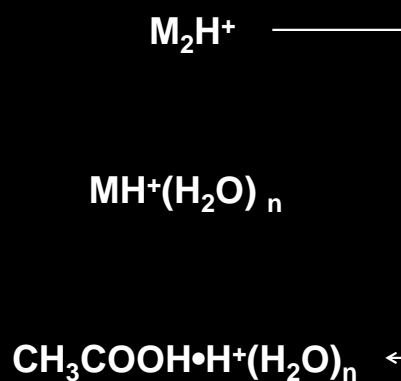
APPEARANCE FIELD FOR FRAGMENT IONS WITH Td AND GAS TEMPERATURE



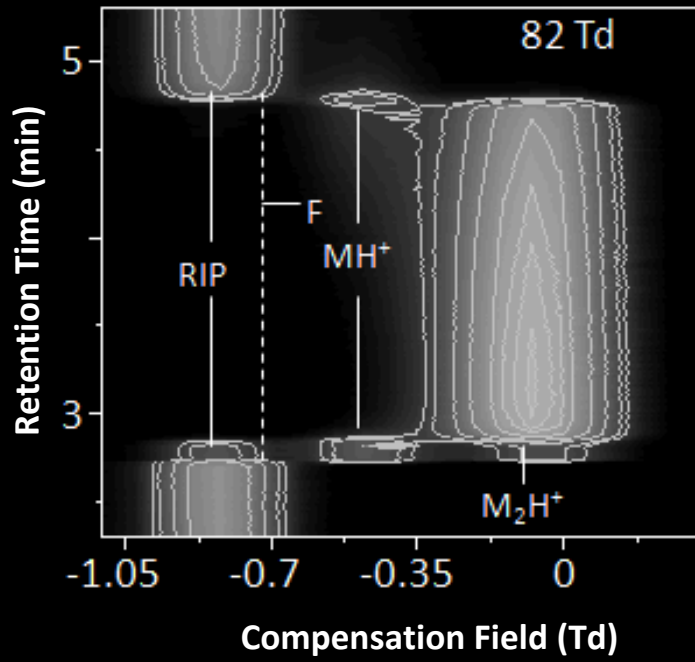
MASS ASSIGNMENT OF DMS MS OF PROPYL ACETATE AT 100°C



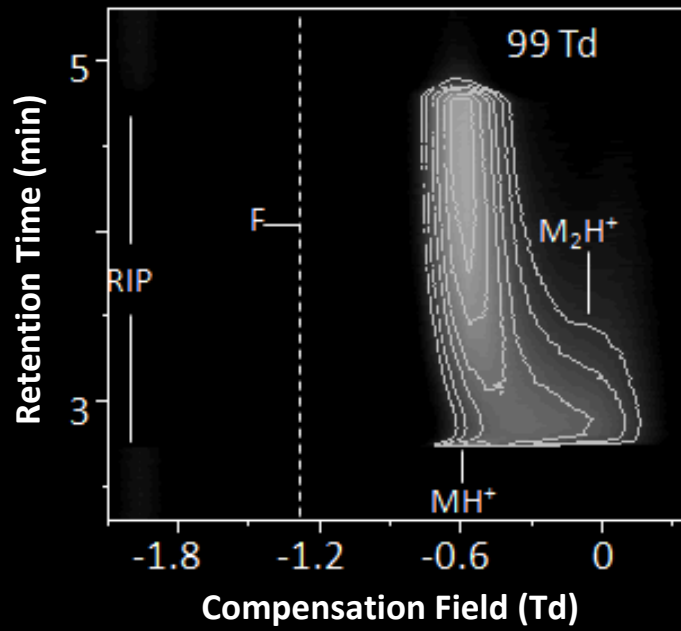
MASS ASSIGNMENT OF DMS MS OF PROPYL ACETATE AT 100°C



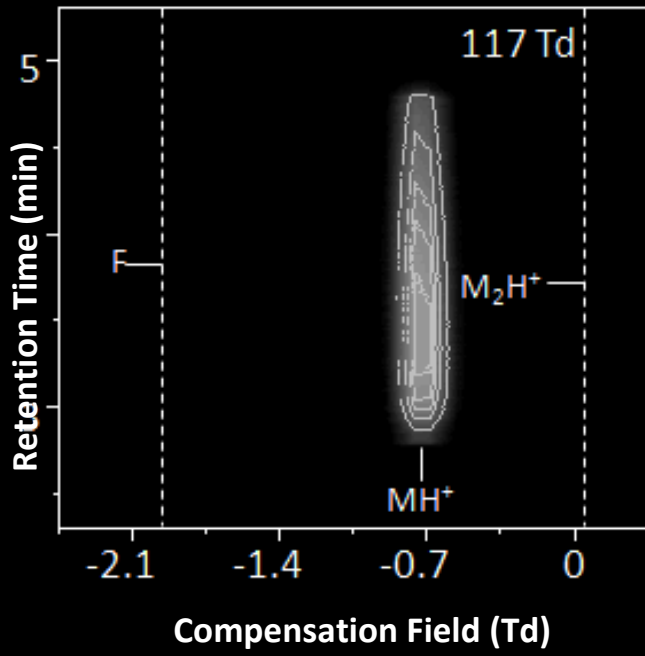
**CONTROL WITH METHYL
ACETATE AT 100°C**



**CONTROL WITH METHYL
ACETATE AT 100°C**



**CONTROL WITH METHYL
ACETATE AT 100°C**



ACKNOWLEDGEMENTS

JAIME RODRIGUEZ
ERKIN NAZAROV

Funding: URI Center for Excellence in Explosives
Detection, Mitigation, and Response