

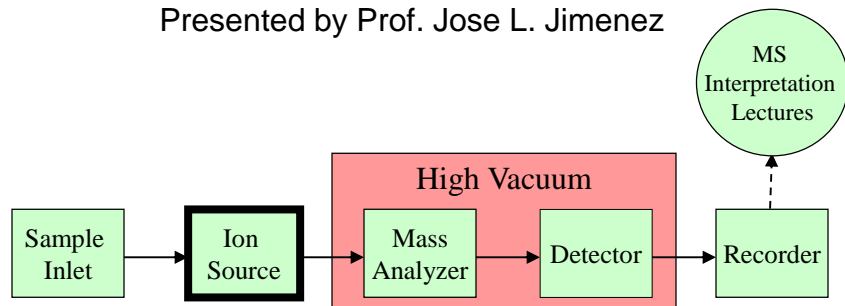
# Ionization 2: Chemical Ionization

CU- Boulder

CHEM-5181

Mass Spectrometry & Chromatography

Presented by Prof. Jose L. Jimenez

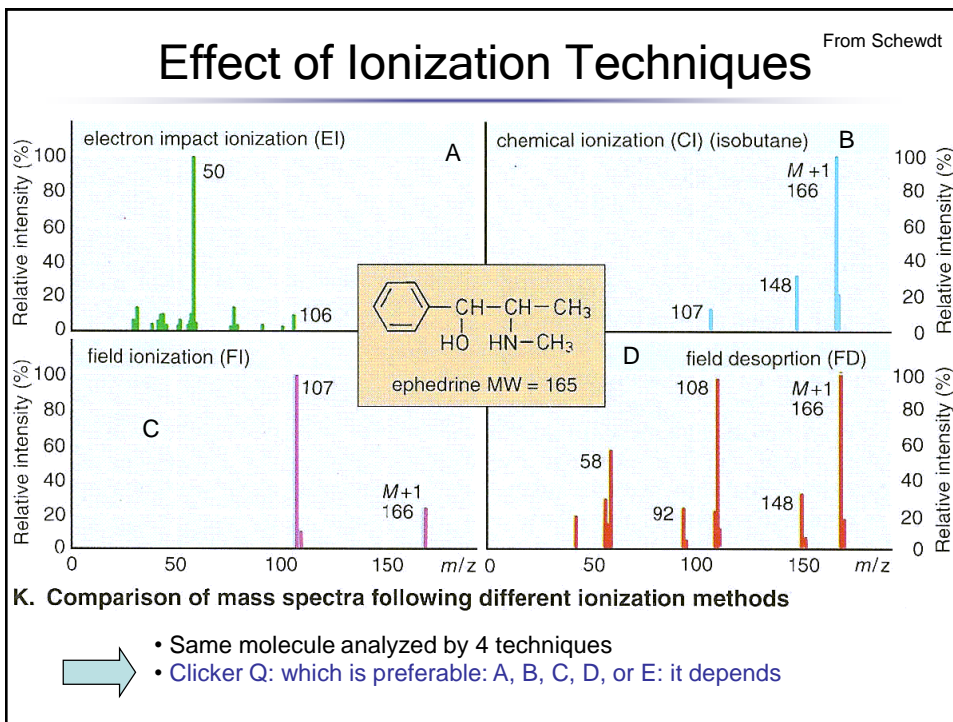


Some slides adapted from Dr. Joel Kimmel's lecture, Fall 2007  
Last updated: Oct. 2014

## Some Commonly Used Ionization Techniques

- Electron Ionization (EI)
- Chemical Ionization (CI)
- Electrospray (ESI) / Nanospray
- Desorption Techniques
  - Matrix-Assisted Laser Desorption/Ionization (MALDI)
  - Fast Atom Bombardment (FAB)
- Ambient: DESI / DART
- Ionization for Elemental Analysis
  - Thermal Ionization Source
  - Spark Source
  - Glow Discharge
  - Inductively-Coupled Plasma (ICP)

*Q: why are so many ionization techniques used in MS?*



## Chemical Ionization (CI)

Introduced in 1966 by Munson and Field<sup>1</sup>, it was a direct outgrowth of fundamental studies of ion/molecule interactions.

Where other techniques rely on interaction of molecule and electron, photon, or electric field, **ionization of the analyte molecule, M, is achieved through reaction with a reagent ion, R<sup>+</sup>**

### CI Method of Munson & Field (Still used)

1. Reagent species is ionized by high-pressure\* electron ionization  

$$e^- + R \rightarrow R^+ + 2 e^-$$
2. Collision of reagent ion with gas-phase analyte (present at <1% abundance of reagent) yields analyte ion  

$$R^+ + M \rightarrow M_1^+ + R_1$$
3. Potential fragmentation of M<sup>+</sup> by one or more pathways  

$$M_1^+ \rightarrow M_2^+ + N_2 \rightarrow M_3^+ + N_3$$

$$\rightarrow M_4^+ + N_4$$

\*: how high P? Remember prob of an electron leading to ionization is  $\sim 3 \times 10^{-7}$  at  $P = 10^{-7}$  Torr

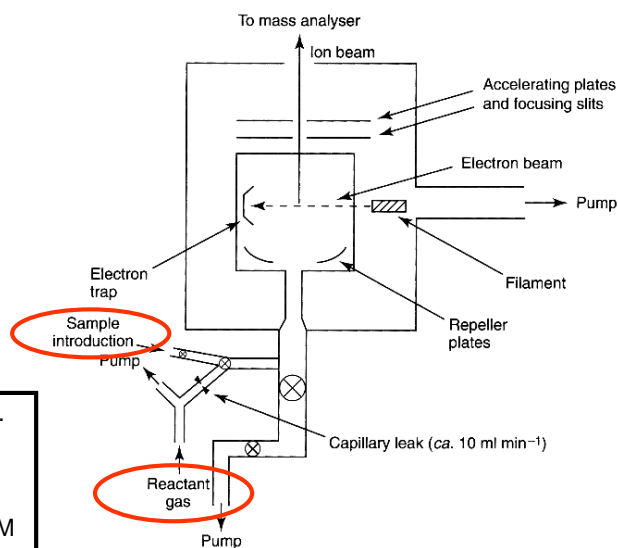
1. Munson and Field, JACS, 2621, 1966. - Suggested reading on course web page

## Clicker Q: Pressure in CIMS?

- If a typical ionizer for atmospheric chemistry CIMS is  $50 \text{ cm}^3$  and with a residence time of 100 ms and a reagent ion mole fraction of 100 ppb, what pressure should it be operated at?
  - 0.1-1 atm
  - 1-100 mbar
  - 0.01-mbar
  - 0.001 mbar
  - I don't know

## CI Ion Source

From Barker



Similar to EI source.

- Higher P
- Simultaneous introduction of M and R

## Combined EI-CI Source

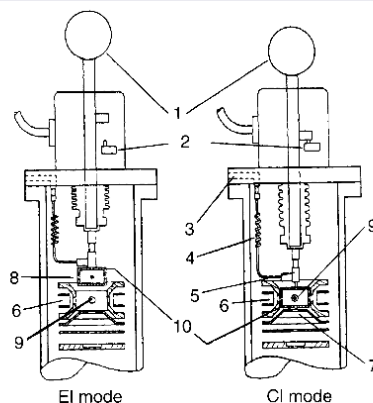


Figure 1.4

Combined EI and CI source. Lowering the box 10 switches from the EI to CI mode: 1, EI/CI switch (in EI mode the box serves as a pusher); 2, micro-switch; 3, entrance for the reagent gas; 4, flexible capillary carrying the reagent gas; 5, diaphragm; 6, filament giving off electrons; 7, path of the ions towards the analyzer inlet; 8, hole for the ionizing electrons in CI mode; 9, sample inlet; 10, box with holes, also named 'ion volume'. (Reproduced from Finnigan MAT 44S documentation, with permission)

## CI Reagents and Products

TABLE 13-8

Reactions Used in CI

From Lambert

Reaction	Reagent*	Reagent Ion*	Product	Thermochemical Property
Proton transfer	<i>i</i> -C <sub>4</sub> H <sub>10</sub>	C <sub>4</sub> H <sub>9</sub> <sup>+</sup>	(M+H) <sup>+</sup>	Proton affinity
Charge exchange	Ar	Ar <sup>++</sup>	M <sup>+</sup>	Ionization energy
Electron capture	CH <sub>4</sub>	e <sup>-</sup>	M <sup>-</sup>	Electron affinity
Cl <sup>-</sup> attachment	CHCl <sub>3</sub> /CH <sub>4</sub>	Cl <sup>-</sup>	(M+Cl) <sup>-</sup>	Cl <sup>-</sup> affinity
Adduct formation	Biacetyl	CH <sub>3</sub> CO <sup>+</sup>	(M+CH <sub>3</sub> CO) <sup>+</sup>	Acetyl affinity
Cluster ion formation	Py	PyH <sup>+</sup>	(M + Py + H) <sup>+</sup>	Molecular pair affinity

\* Examples given are typical cases; many other choices can be made.

- Many different chemistries used depending of what one wants
- A CU ANYL student developed a new chemistry as part of his PhD:
  - $\text{CH}_3\text{-COO}^- + \text{R-COOH} \rightarrow \text{CH}_3\text{COOH} + \text{R-COO}^-$ 
    - proton abstraction by acetate ion
    - Veres, P., J.M. Roberts, C. Warneke, D. Welsh-Bon, M. Zahniser, S. Herndon, R. Fall, and J. de Gouw, Development of Negative-Ion Proton-Transfer Chemical-Ionization Mass Spectrometry (NI-PT-CIMS) for the Measurement of Gas-Phase Organic Acids in the Atmosphere, *Int. J. Mass Spectrom.*, 274, 48-55, doi:10.1016/j.ijms.2008.04.032, 2008.
    - <http://dx.doi.org/10.1016/j.ijms.2008.04.032>
    - Used by multiple groups now, including ours

## Gas-Phase Ion-Molecule Reactions

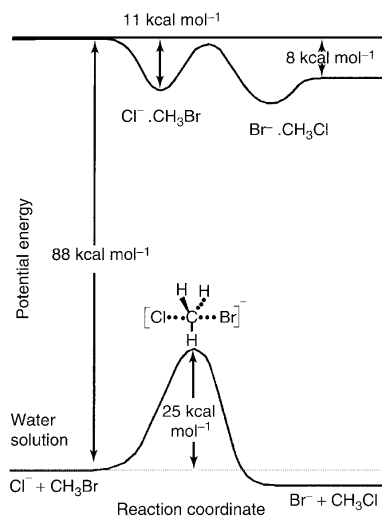
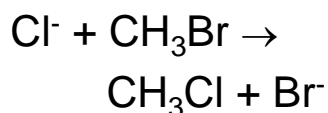
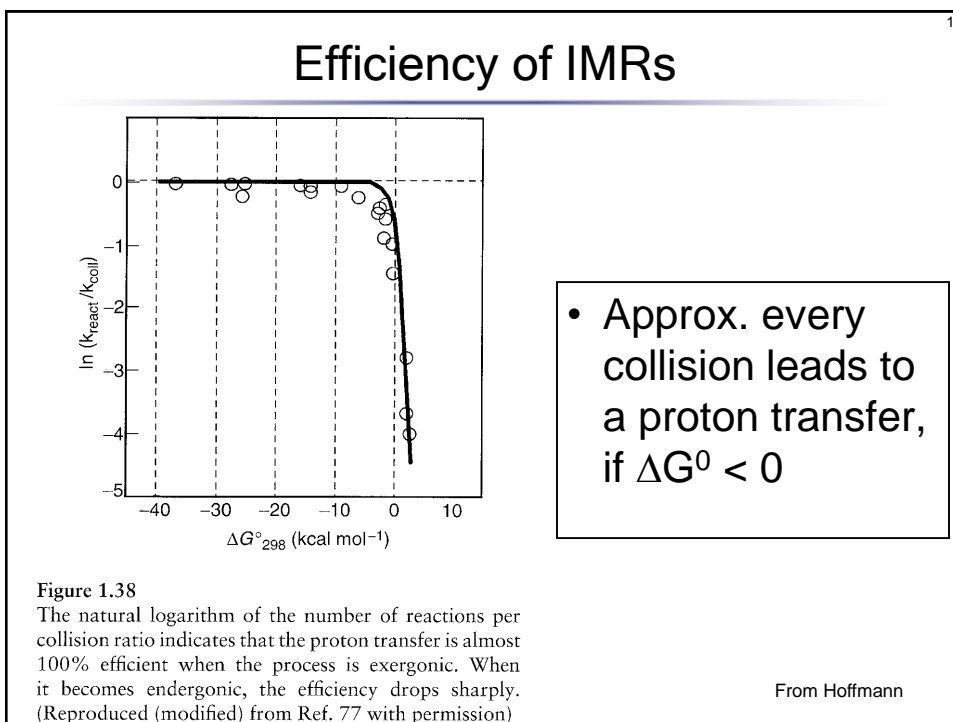
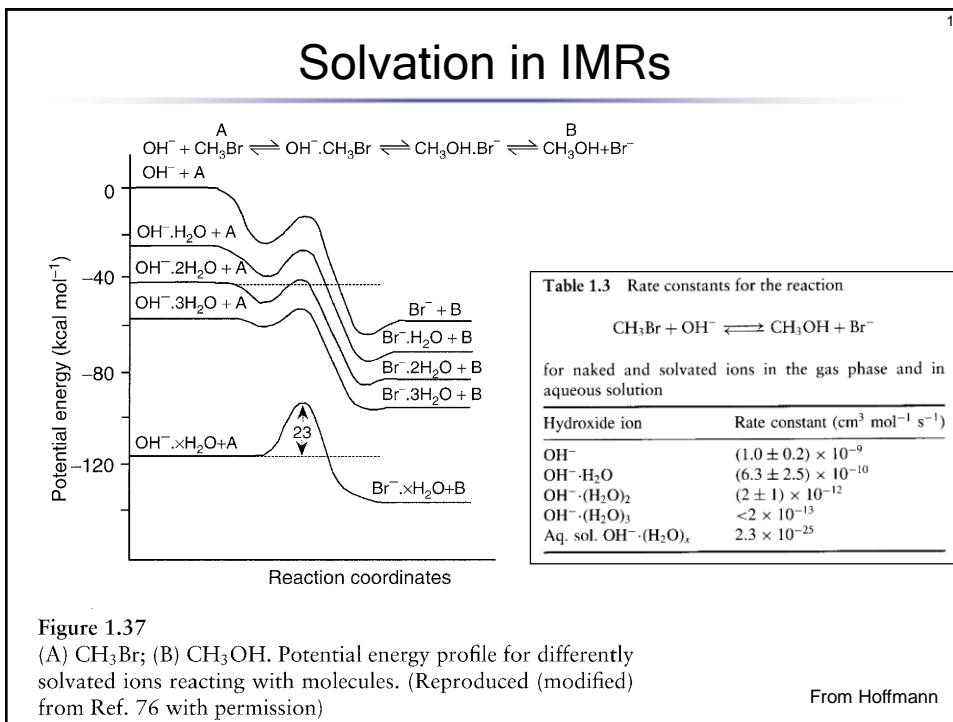


Figure 1.36  
Potential energy diagram for a substitution reaction in the gas phase and in solution in water<sup>75</sup>

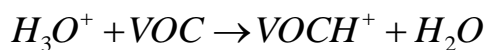
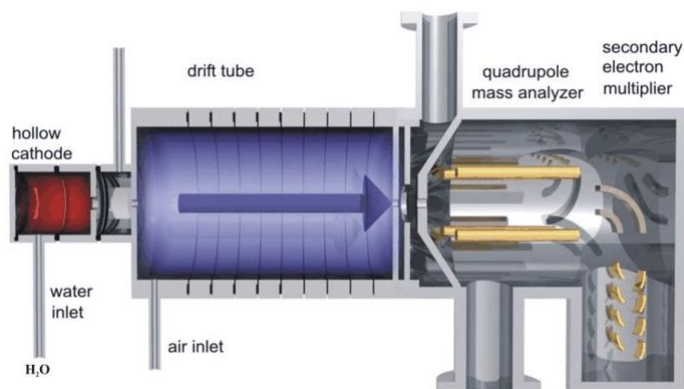
From Hoffmann

## Gas-Phase IMRs Notes

- Condensed Phase
  - Molecules are strongly solvated
  - Ions even more so
  - High activation energies to break the solvation cage
  - Also continuous exchange of energy from collisions
- Gas Phase
  - Interaction of naked ion with molecule is exothermic
    - Ion-molecule complex formation
  - Energy remains in the complex due to lack of collisions (low-pressure), allowing it to overcome the barrier
  - Non-equilibrium!!



## Proton transfer reaction - mass spectrometry



$$PA(VOC) > PA(H_2O)$$

Courtesy of Lisa Kaser, NCAR

## Clicker Question

$$\Delta H_{\text{react}} = PA(H_2O) - PA(VOC)$$

The reaction will proceed if:

- (a) If  $\Delta H$  is VERY, VERY POSITIVE
- (b) If  $\Delta H$  is POSITIVE
- (c) If  $\Delta H$  is NEGATIVE
- (d) If  $\Delta H$  is zero
- (e) If  $\Delta H$  is VERY, VERY NEGATIVE

Note: PA = Proton Affinity: energy released (or absorbed if  $< 0$ ) when a proton attaches to a molecule

– Note sign convention is reversed!

# Proton Affinities

Table 1  
Volatile substances, their chemical formulae and molecular (atomic) masses; column 5 shows the product ion masses detected after reactions with  $H_3O^+$ ; column 6 shows the proton affinities, and the two last columns show the measured and calculated rate coefficients for reactions of the volatile substances with  $H_3O^+$  ions

No.	Substance	Formula	Mass	Detected ionic products (mass)	Proton affinity <sup>a</sup> / kcal mol <sup>-1</sup>	Measured thermal rate constant <sup>b</sup> / 10 <sup>-9</sup> cm <sup>3</sup> s <sup>-1</sup>	Calculated thermal rate constant <sup>c</sup> / 10 <sup>-9</sup> cm <sup>3</sup> s <sup>-1</sup>
1	Helium	He	4	—	42.5	—	—
2	Neon	Ne	20	—	48.6	—	—
3	Argon	Ar	40	—	58.2	—	—
4	Oxygen	O <sub>2</sub>	32	—	100.6	—	—
5	Hydrogen	H <sub>2</sub>	2	—	100.9	—	—
6	Krypton	Kr	84	—	101.5	—	—
7	Nitrogen	N <sub>2</sub>	28	—	118.0	—	—
8	Xenon	Xe	132	—	118.6	—	—
9	Carbon dioxide	CO <sub>2</sub>	44	—	129.2	—	—
10	Carbon monoxide	CO	28	—	141.7	—	—
11	<b>Water</b>	<b>H<sub>2</sub>O</b>	<b>18</b>	—	<b>165.2</b>	—	—
12	Hydrogen sulphide	H <sub>2</sub> S	34	35	168.5	1.4	1.9
13	Formaldehyde	CH <sub>2</sub> O	30	31	170.4	3.0	3.3
14	Formic acid	CH <sub>2</sub> O <sub>2</sub>	46	47	177.3	2.7	2.2
15	Benzene	C <sub>6</sub> H <sub>6</sub>	78	79	179.3	2.1	1.9
16	Propene	C <sub>3</sub> H <sub>6</sub>	42	43	179.6	1.5	1.7
17	Methanol	CH <sub>3</sub> O	32	33	180.3	2.2	2.7
18	Acetaldehyde	C <sub>2</sub> H <sub>4</sub> O	44	45	183.8	3.6	3.7
19	Ethanol	C <sub>2</sub> H <sub>5</sub> O	46	47	185.6	2.8	2.7
20	Acetonitrile	C <sub>2</sub> H <sub>3</sub> N	41	42	186.2	4.7	5.1
21	Toluene	C <sub>7</sub> H <sub>8</sub>	92	93	187.4	2.1	2.2
22	Propanal	C <sub>3</sub> H <sub>4</sub> O	58	59	187.6	—	3.6
23	Propan-1-ol	C <sub>3</sub> H <sub>7</sub> O	60	43(80%) 61(20%)	188.2	2.3	2.7
24	Butanal	C <sub>4</sub> H <sub>8</sub> O	72	73(65%) 55(35%)	189.5	—	3.8
25	Xylene	C <sub>8</sub> H <sub>10</sub>	106	107	190.0	—	2.2
26	Propan-2-ol	C <sub>3</sub> H <sub>7</sub> O	60	43(90%) 61(10%)	190.1	2.8	2.8
27	Acetic acid	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	60	61	190.2	3.0	2.7
28	1,4-Dioxane	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	88	89(80%) 45(20%)	190.7	—	1.9
29	Acetone	C <sub>3</sub> H <sub>6</sub> O	58	59	194.1	3.9	3.9
30	Phenol	C <sub>6</sub> H <sub>5</sub> O	94	95	195.0	—	2.7
31	Dimethyl sulphide	C <sub>2</sub> H <sub>6</sub> S	62	63	198.6	2.1	2.6
32	Isoprene	C <sub>5</sub> H <sub>8</sub>	68	69	198.9	1.3	2.0
33	Ammonia	NH <sub>3</sub>	17	18	204.1	2.2	2.6

<http://www.sciencedirect.com/science/article/pii/S0168117697002814>  
<http://www.kore.co.uk/baffinities.htm>  
[http://en.wikipedia.org/wiki/Proton\\_affinity\\_\(data\\_page\)](http://en.wikipedia.org/wiki/Proton_affinity_(data_page))

W. Lindinger et al. *International Journal of Mass Spectrometry and Ion Processes* 173 (1998) 191–241

## Reagent Gases Used in H<sup>+</sup> Addition CI

TABLE 8.1. Characteristics of reagent gases for CI

Reagent gas	Predominant reactant ions	Proton affinity <sup>a</sup> (kcal/mol)	Hydride affinity (kcal/mol)
He/H <sub>2</sub>	HeH <sup>+</sup>	42	—
H <sub>2</sub>	H <sup>3+</sup>	101.2	300
CH <sub>4</sub>	CH <sub>5</sub> <sup>+</sup>	131.6	269
	C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	159	271
H <sub>2</sub> O	H <sub>3</sub> O <sup>+</sup>	166.5	—
CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	C <sub>3</sub> H <sub>7</sub> <sup>+</sup>	182	270
CH <sub>3</sub> OH	CH <sub>3</sub> OH <sub>2</sub> <sup>+</sup>	182 <sup>b</sup>	—
(CH <sub>3</sub> ) <sub>3</sub> CH (isobutane)	C <sub>4</sub> H <sub>9</sub> <sup>+</sup>	196 <sup>c</sup>	266
NH <sub>3</sub>	NH <sub>4</sub> <sup>+</sup> , (NH <sub>3</sub> ) <sub>2</sub> H <sup>+</sup> , (NH <sub>3</sub> ) <sub>3</sub> H <sup>+</sup>	204.0	—
(CH <sub>3</sub> ) <sub>2</sub> NH	(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> <sup>+</sup> , (CH <sub>3</sub> ) <sub>2</sub> H <sup>+</sup> , C <sub>3</sub> H <sub>8</sub> N <sup>+</sup>	220.6	—
(CH <sub>3</sub> ) <sub>3</sub> N	(CH <sub>3</sub> ) <sub>3</sub> NH <sup>+</sup>	225.1	—

<sup>a</sup>Lias SG, Bartmess JE, Liebman JF, Holmes JL, Levin RD, Mallard WG. *J Phys Chem Ref Data* 1988;17(suppl 1).

<sup>b</sup>Harrison AG. *Chemical Ionization Mass Spectrometry*, ed 2. CRC Press, Boca Raton, Fla., 1992.

<sup>c</sup>Proton affinity of isobutylene, which is the conjugate base of isobutane.

From Watson



### Clicker Question

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PA(methane) = 5.7 eV

PA(isobutane) = 8.5 eV

The analyte molecule M is known to be ionized by a proton transfer mechanism with both methane or isobutane. **Which of the options below is true?**

- (A)  $PA(M) > 8.5 \text{ eV}$
- (B)  $5.7 \text{ eV} < PA(M) < 8.5 \text{ eV}$
- (C)  $PA(M) < 5.7 \text{ eV}$
- (D) None of the above
- (E) I don't know

### Clicker Question

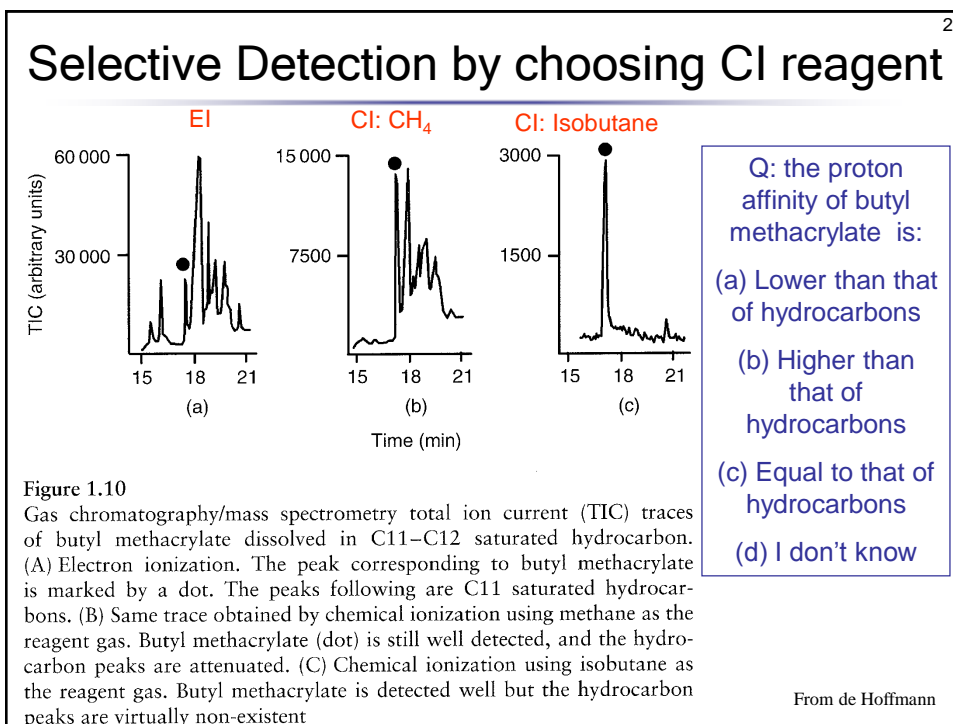
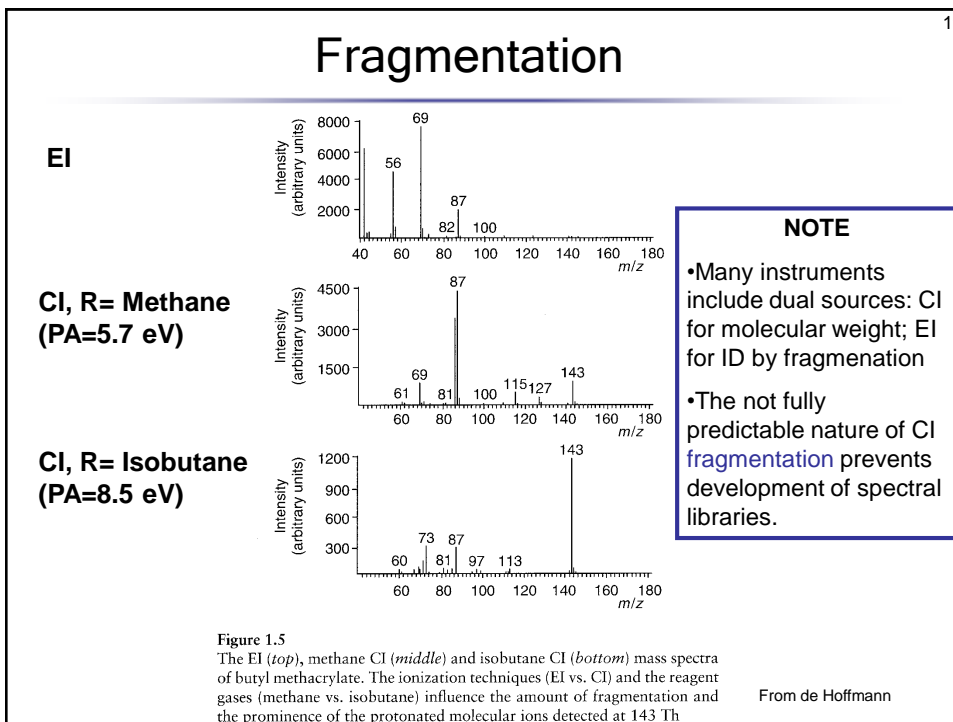
18

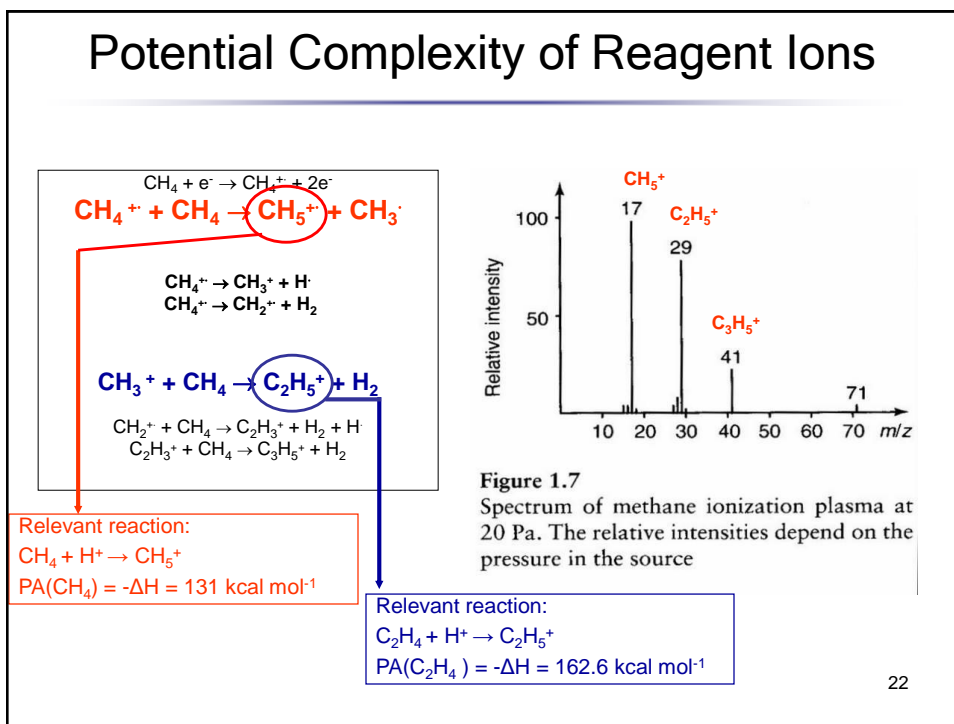
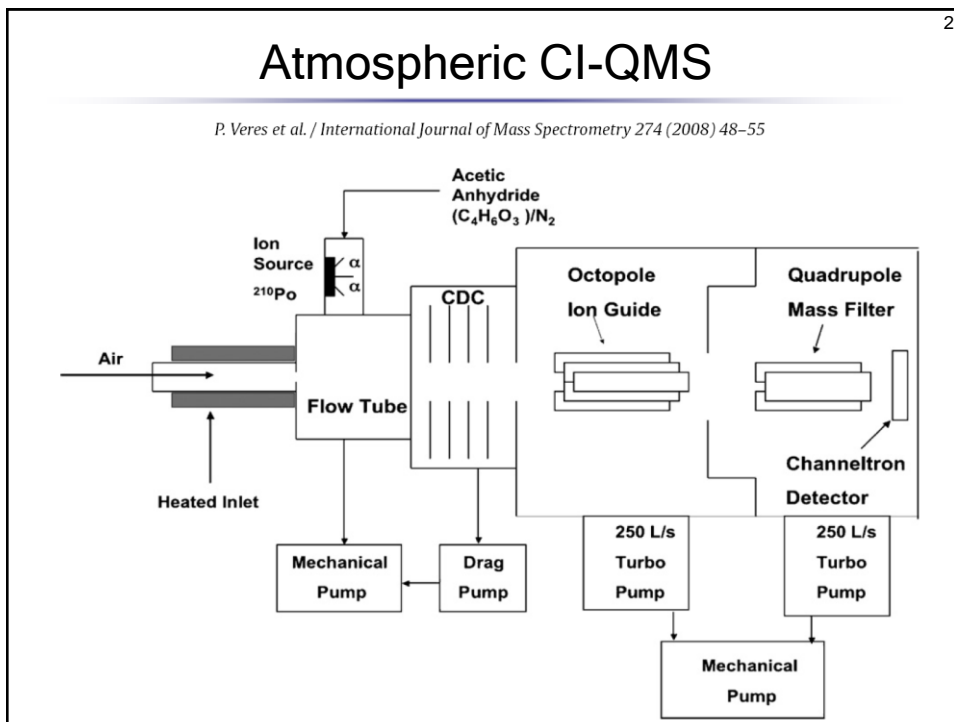
PA(methane) = 5.7 eV

PA(isobutane) = 8.5 eV

**Which reagent gas is more likely to yield fragmentation of M?**

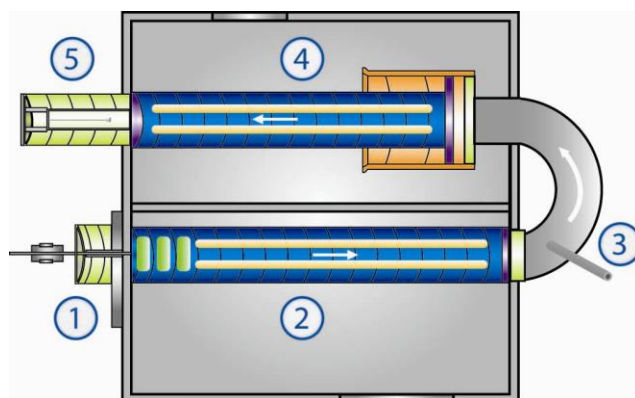
- (A) Isobutane
- (B) Methane
- (C) Depends on structure of M
- (D) It cannot be determined without additional info
- (E) I don't know





## Selected Ion Flow Tube & SYFT MS

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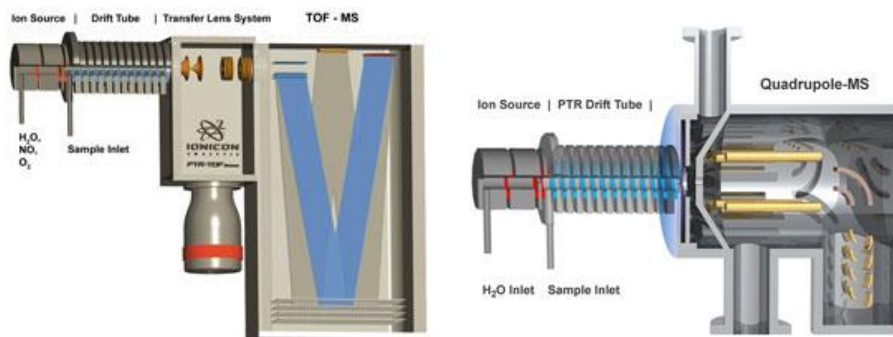


**syft**<sup>TM</sup>  
Technologies  
<http://www.syft.com/>

1. Generation of ions
2. Ion selection:  $\text{H}_3\text{O}^+$ ,  $\text{NO}^+$  and  $\text{O}_2^+$
3. Sample introduction and reaction
4. Selection of reaction products
5. Detection.

## Proton-Transfer Reaction MS

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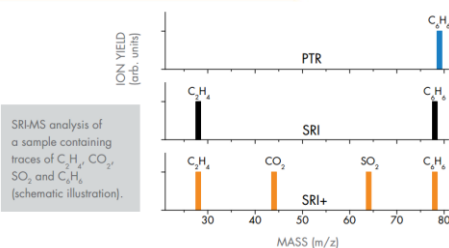
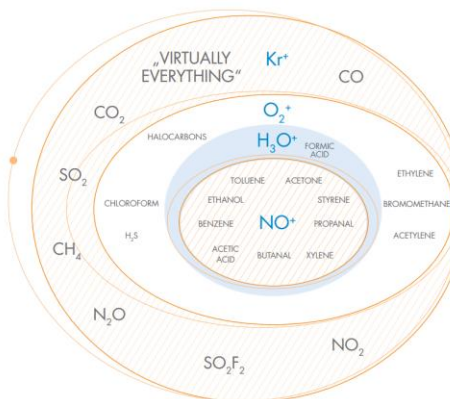


**IONICON**  
ANALYTIX

<http://www.ptrms.com/>

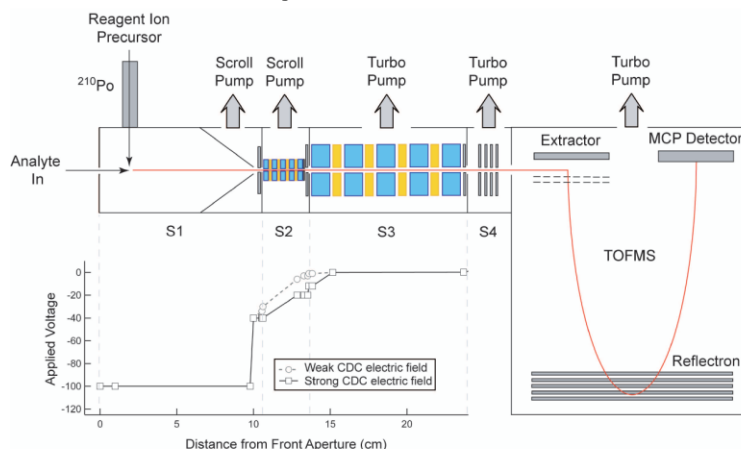
## Switchable Reagent Ions in PTRMS

REAGENT ION	IONICON TECHNOLOGY	MAIN BENEFITS, DETECTABLE SUBSTANCES AND EXAMPLES
$\text{H}_3\text{O}^+$	PTR-MS	Most common volatile organic compounds (VOCs); e.g. aldehydes, ketones, acids, esters, alcohols, aromatic compounds, nitriles, amines, amides, thiols, sulfides, with a detection limit down to the sub-pptv-range.
$\text{NO}^+$	SRI	Similar to $\text{H}_3\text{O}^+$ , especially advantageous for the separation of aldehydes and ketones, carboxylic acids and esters, carboxylic acids and alcohols, etc.
$\text{O}_2^+$	SRI	Additionally e.g. ethylene and acetylene and nearly all halocarbons (carbon with fluorine, chlorine, bromine and iodine) can be detected.
$\text{Kr}^+$	SRI+	The Universal Trace Gas Analyzer: e.g. $\text{CO}$ , $\text{CO}_2$ , $\text{SO}_2$ , $\text{CH}_4$ , $\text{N}_2\text{O}$ and all above mentioned can be detected with IONICON instruments incl. SRI+.



[http://www.ionicon.com/sites/default/files/uploads/doc/other\\_flyer\\_ionicon\\_sri.pdf](http://www.ionicon.com/sites/default/files/uploads/doc/other_flyer_ionicon_sri.pdf) (Nov 2013)

## Aerodyne ToF-CIMS



**Fig. 1.** Schematic of the chemical ionization source and four stage (S1-S4) differentially pumped interface coupled to the time-of-flight mass spectrometer (TOFMS,  $5 \times 10^{-7}$  mbar). The high pressure interface consists of: (i) ion-molecule reaction (IMR) chamber (S1, 85 mbar), (ii) collisional dissociation chamber (CDC) (S2, 2 mbar), (iii) stage 3 that houses a second RF-only segmented quadrupole (S3,  $1.5 \times 10^{-2}$  mbar), and (iv) stage 4 that houses a series of DC optics that focus and accelerate the primary beam into the TOFMS (S4,  $3.5 \times 10^{-5}$  mbar). DC voltages applied to the focusing electrodes under two different declustering conditions, are shown in the inset figure, as a function of the distance from the entrance aperture.

Bertram, T. H., Kimmel, J. R., Crisp, T. A., Ryder, O. S., Yatavelli, R. L. N., Thornton, J. A., Cubison, M. J., Gonin, M., and Worsnop, D. R.: A field-deployable, chemical ionization time-of-flight mass spectrometer, *Atmos. Meas. Tech.*, 4, 1471-1479, doi:10.5194/amt-4-1471-2011, 2011

