

# Fundamental ion-molecule reaction studies at elevated ion temperature and analytical application of an ion activation stage ("ion tunnel")

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## Motivation

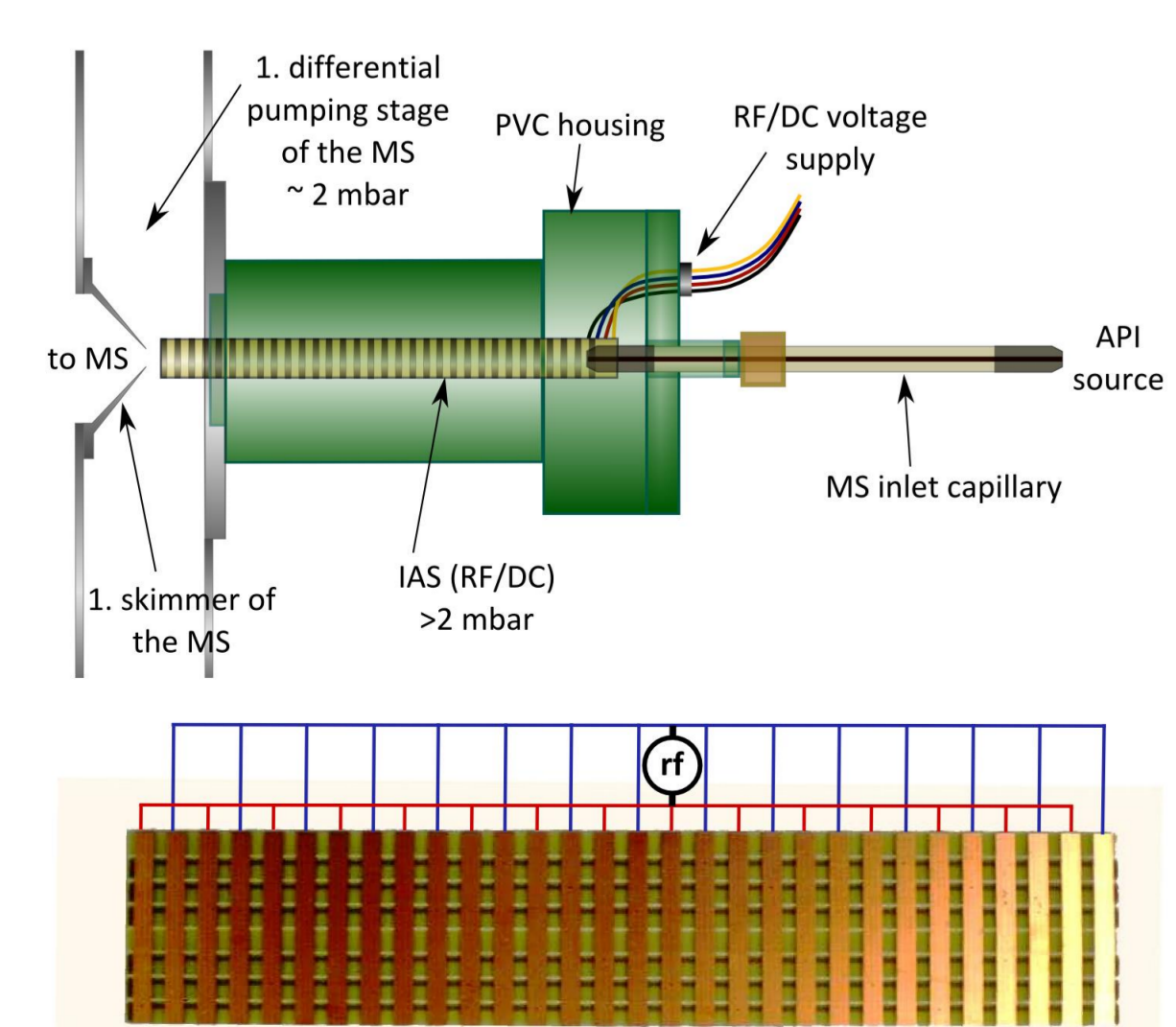
### Ion temperature – a critical parameter in API

Ionization methods operating at atmospheric pressure (API) have largely affected the development of analytical mass spectrometry. Virtually every API mass spectrometer on the market – regardless of type – is compatible with numerous API methods, the most prominent being ESI, APCI, and APPI sources. Despite the ease of use and rapid exchangeability of such sources, ions generated at elevated pressure have to be efficiently transported through a pressure gradient generally spanning more than 9 orders of magnitude. The present research efforts are addressing such issues as:

- Ions generated at AP are generally subjected to at least  $10^7$  molecular collisions before they reach the essentially collision-free vacuum region.
  - How do these collisions potentially alter the ion population distribution recorded?
- Ion-molecule reactions occurring at AP are generally thermodynamically controlled. The temperature driving corresponding equilibria is close to or slightly above room temperature, despite the considerable amounts of heat transported via gas flows (e.g., "desolvation" or "nebulization" gas flows) into the source region. At AP, electrical fields hardly affect this equilibrium chemistry. This changes dramatically when the mean free molecular path increases but collision numbers are still high (i.e., beginning in the the low mbar regime).
  - What is the impact of electrical fields on the ion temperature and thus on chemical equilibria and/or individual bimolecular reactions?
  - Is it possible to control the amount of kinetic energy supplied to the ions within the collision dominated regions? To what extent is such control possible?
  - Is there a way to make analytical use of such control?

## Methods

**MS:** Bruker Daltonics micrOTOF; Hiden Analytical HPR-60 quadrupole mass spectrometer  
**Ion Source:** Custom cAPCI + c(DA) APPI sources  
**RF Activation:** Custom RF stage 15 cm long;  $RF_{max}$  200 V<sub>pp</sub>; operating pressure = 1 ... 20 mbar. Critically operated glass capillary as flow restrictor; d = 0.5 mm; length 20 cm ("ion tunnel")  
**Simulation:** ChemKed II Version 3.3



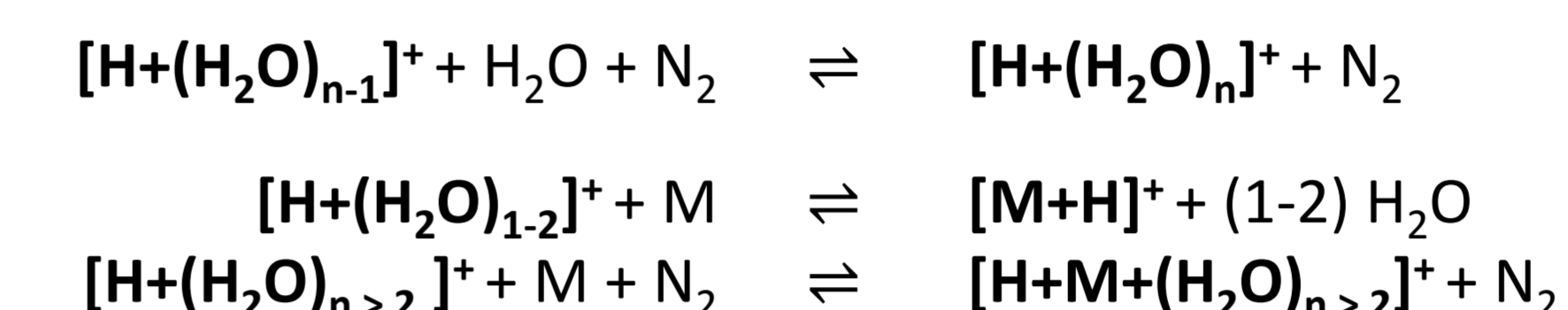
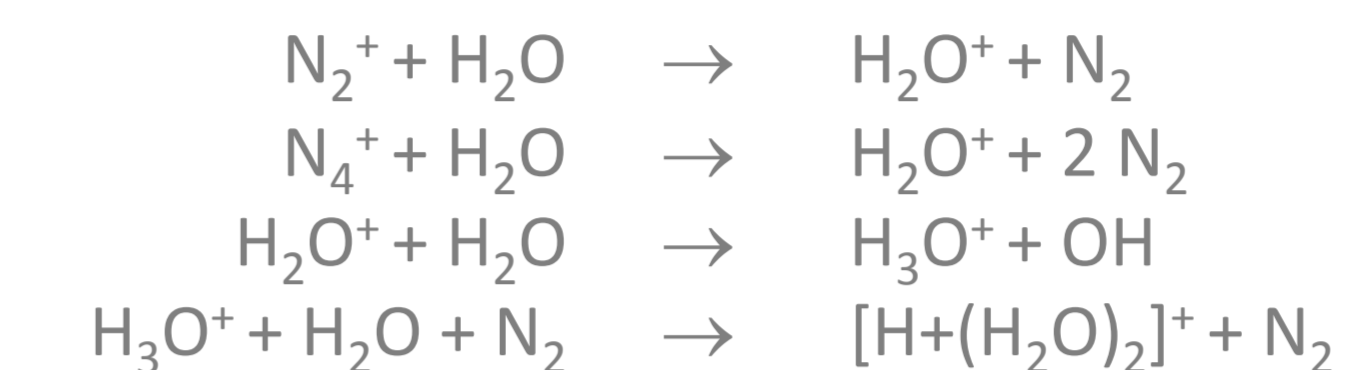
- Ion tunnel mounted to either the Hiden or micrOTOF instrument. The API source was either a corona discharge or VUV light driven stage.
- Printed circuit board structure used for the construction of the tunnel (unfolded). For operation, the structure is folded to a hexagonal geometry. The capillary exit can be positioned anywhere in the tunnel structure.

## Significance of the proton bound water cluster system

### The proton bound water cluster system

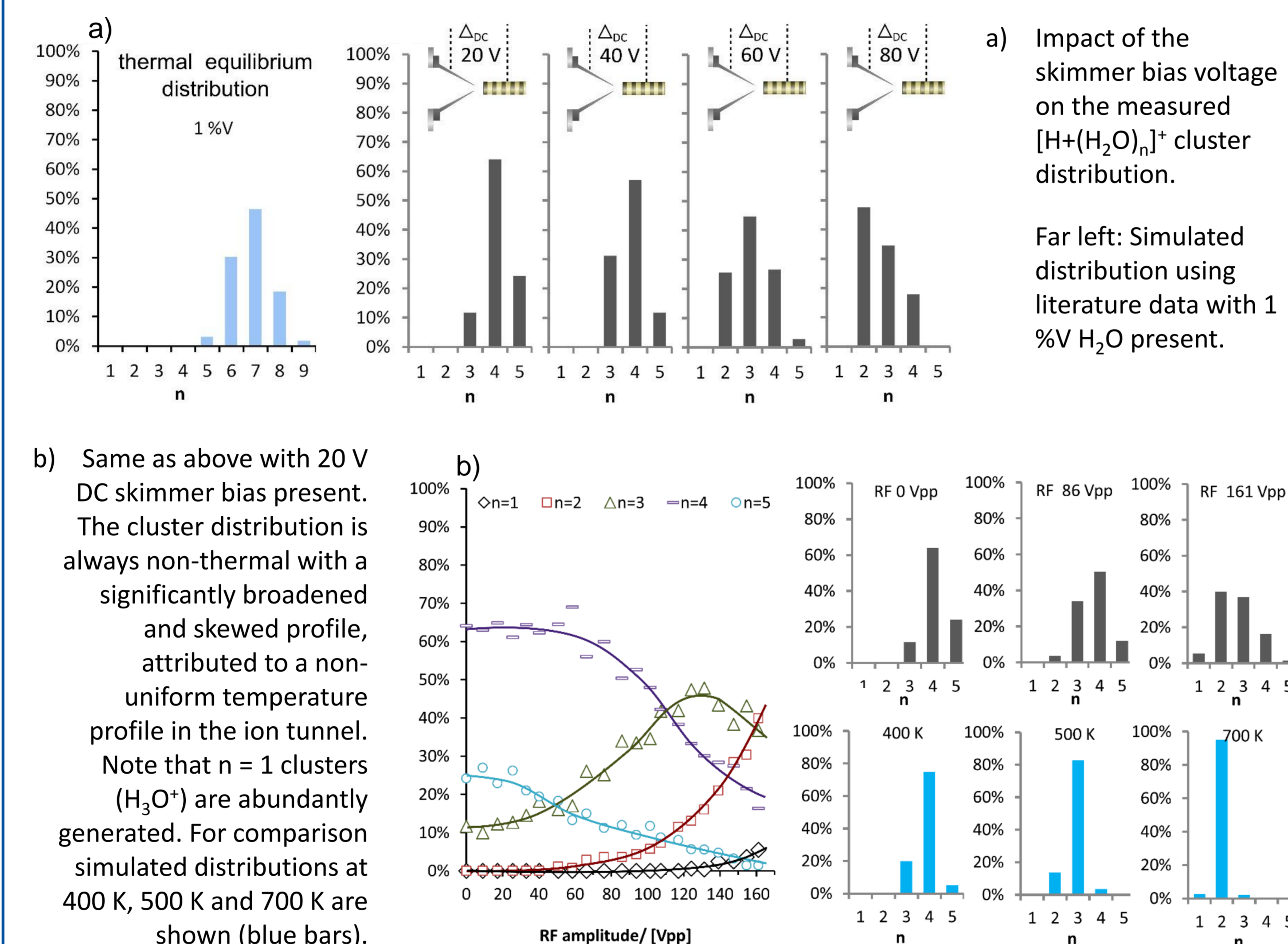
The majority of all API methods operating in the gas phase (APCI, APPI, and the dopant assisted (DA) varieties, as well as many ambient ionization methods) lead to protonated analyte molecules. It has been repeatedly shown that proton bound water (or "solvents" where applicable) clusters are the proton donors via cluster chemistry. The closely coupled cluster reaction system comprised of several fast equilibria readily adjusts as a whole to the prevailing local temperature and represents thus a favorable "equilibrium thermometer".

The reaction pathway for the generation of protonated molecules (bimolecular collision vs. thermal cluster chemistry) depends on the proton bound cluster sizes, thus the field dependent cluster distribution is of analytical interest.

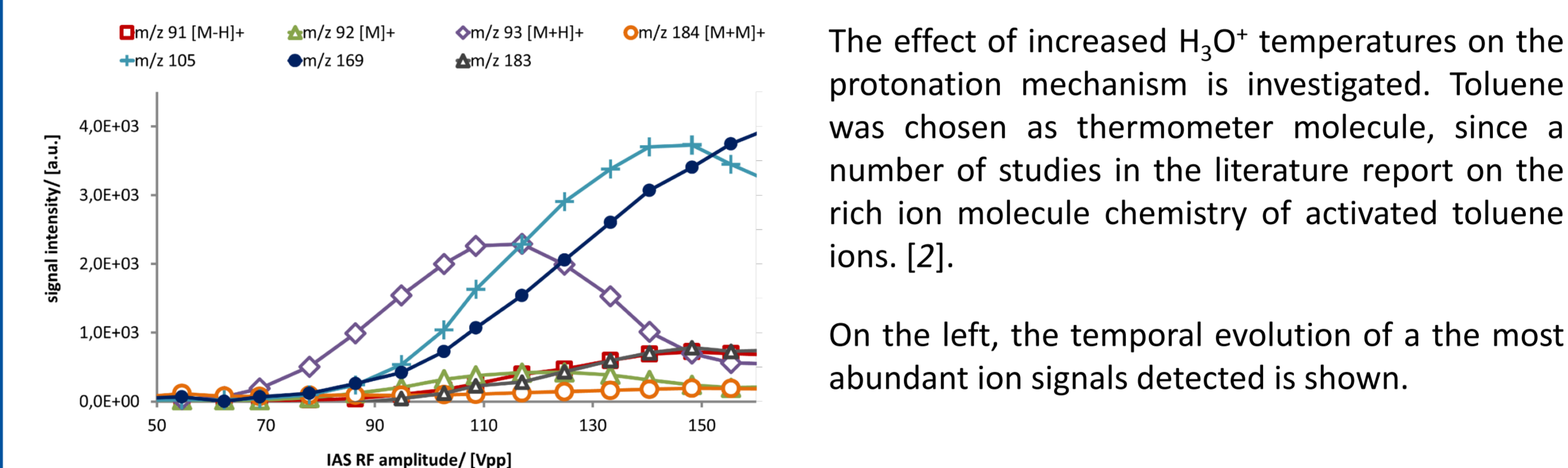


## Experimental results

### The proton bound water cluster system



### Dissociative Proton Transfer Induced Ion Molecule Chemistry



The effect of increased  $H_3O^+$  temperatures on the protonation mechanism is investigated. Toluene was chosen as thermometer molecule, since a number of studies in the literature report on the rich ion molecule chemistry of activated toluene ions. [2].  
 On the left, the temporal evolution of a the most abundant ion signals detected is shown.

Using tunnel RF activation, the presence of  $H_3O^+$  is inevitably tied to strongly elevated ion temperatures:  
 The simulated ion temperature for noticeable  $H_3O^+$  generation from an equilibrated proton bound water cluster distribution in the presence of 1 %V  $H_2O$  mixing ratio is roughly 700 K.  
 The protonation of toluene with  $H_3O^+$  (R2a) becomes progressively dissociative at temperatures above 900 K and reaches a branching ratio of about 0.5 at  $T = 1200$  K

$$\begin{aligned} C_6H_5CH_3 + H_3O^+ &\rightarrow [C_6H_5CH_3 + H]^+ + H_2O && ([M+H]^+; m/z 93) && (R2a) \\ &\rightarrow C_6H_5CH_2^+ + H_2O + H_2 && ([M-H]^+; m/z 91; T > 900K) && (R2b) \\ &\rightarrow C_7H_7^+ + H_2O + H_2 && ([M-H]^+; m/z 91; T > 900K) && (R2c) \end{aligned}$$

The dissociative channel generating  $[M-H]^+$  is further branched to yield rather reactive benzylium ions (R2b) and less reactive tropylium ions (R2c).

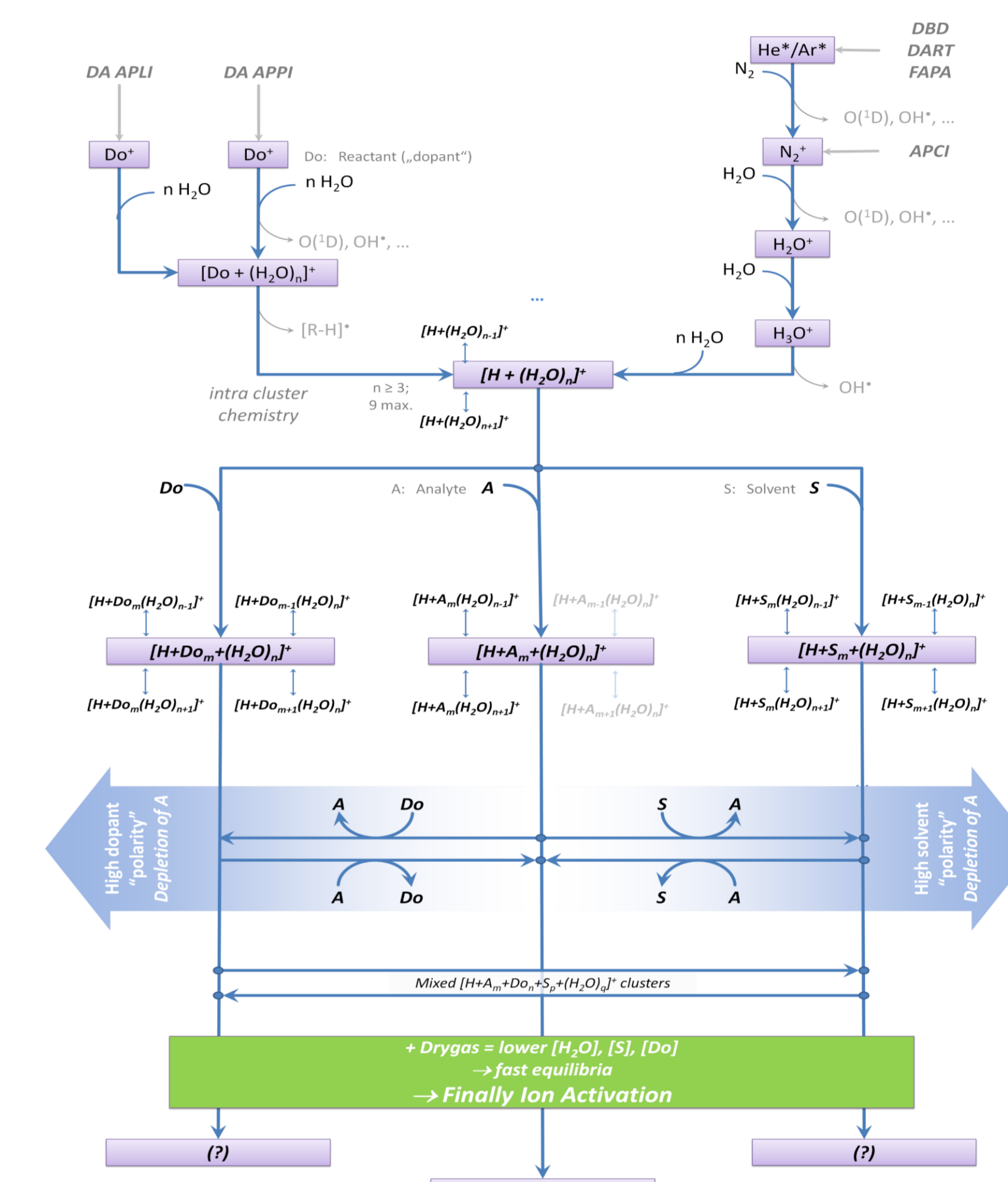
- The distinct onset of ion formation with m/z ratios larger than that of protonated toluene (i.e., m/z 105, 163, 183) at 80 V<sub>pp</sub> is induced by reactions of benzylium and phenyl ions with neutral toluene, as described in [2]:
 
$$\begin{aligned} C_6H_5CH_2^+ + C_6H_5CH_3 &\rightarrow C_8H_9^+ + C_6H_6 && (m/z 105) && (R3) \\ C_6H_5^+ + C_6H_5CH_3 &\rightarrow C_{13}H_{13}^+ && (m/z 169) && (R4) \\ C_6H_5CH_2^+ + C_6H_5CH_3 &\rightarrow [C_6H_5CH_2 + C_6H_5CH_3]^+ && (m/z 183) && (R5) \end{aligned}$$
- The rather small yields of m/z 91 ( $[M-H]^+$ ) ions, which are most probably unreactive tropylium ions.
- The pronounced transient nature of the m/z 93 ( $[M+H]^+$ ) signal is due to collisionally induced fragmentation of protonated toluene molecules at elevated RF voltages [3].
- The generation of toluene radical cations (m/z 92) caused by charge exchange with ionic fragments, e.g. via R20b among many other possible routes [2].
- The subsequent formation of toluene radical cation dimers (m/z 184) according to the monomer-dimer equilibrium system [2].

## Literature

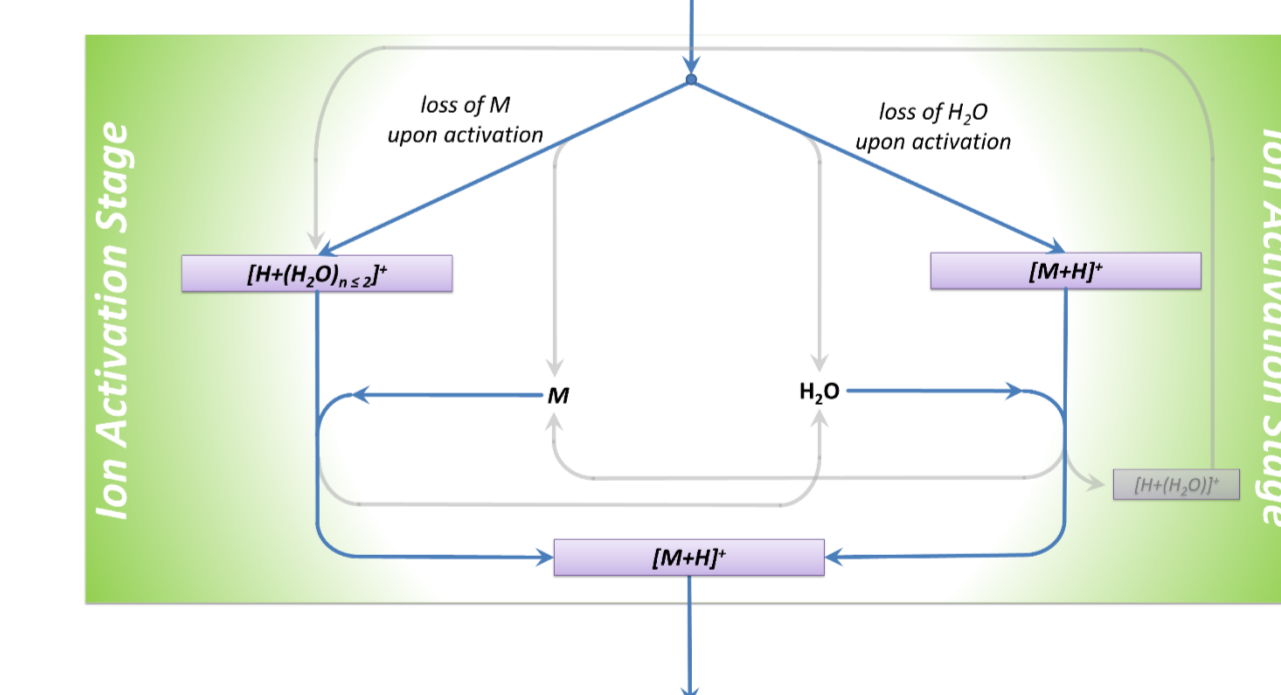
[1] Spänzel, P.; Smith, D. Selected ion flow tube studies of the reactions of  $H_3O^+$ ,  $NO^+$ , and  $O_2^+$  with some chloroalkanes and chloroalkenes. *Int. J. Mass Spectrom.* 1999, 184, 175 – 181.  
 [2] Wexler, S.; Clow, R. P. Ion-Molecule Reactions in Gaseous Benzene and Toluene. *J. Am. Chem. Soc.* 1968, 90, 3940 – 3945.  
 [3] Schröder, D.; Schwarz, H.; Milko, P.; Roithova, J. Dissociation Routes of Protonated Toluene Probed by Infrared Spectroscopy in the Gas Phase. *J. Phys. Chem. A* 2006, 110, 8346 – 8353.

## Conclusions

On the basis of the presented experimental and modeling results, a comprehensive thermal API chemistry for ionization methods operating in the gas phase (i.e. within the AP ion source) is proposed:



Furthermore, the above scheme is expanded to non-thermal conditions encountered during ion transfer towards the collision free analyzer region as shown below:



- These findings clearly demonstrate the impact of the ion temperature on the ion chemistry prevailing in pressure regions which are collisionally dominated.
- Within the tunnel, collision rates of the order of at least  $10^6$  s<sup>-1</sup> lead to significant ion activation, which not only shifts cluster equilibria but also drives bimolecular processes.
- The operation of an ion activation stage between capillary exit and the first sampling stage of API mass spectrometers may thus find several applications such as reagent ion preparation with carefully adjusted reactivity, controlled cluster decomposition, and even controlled covalent bond cleavage.

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