Supporting Information.

Time of flight mass spectrometry for quantitative data analysis in fast transient studies using a Temporal Analysis of Products (TAP) reactor

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Figure S1: SIMION ion optical model of the ion source.

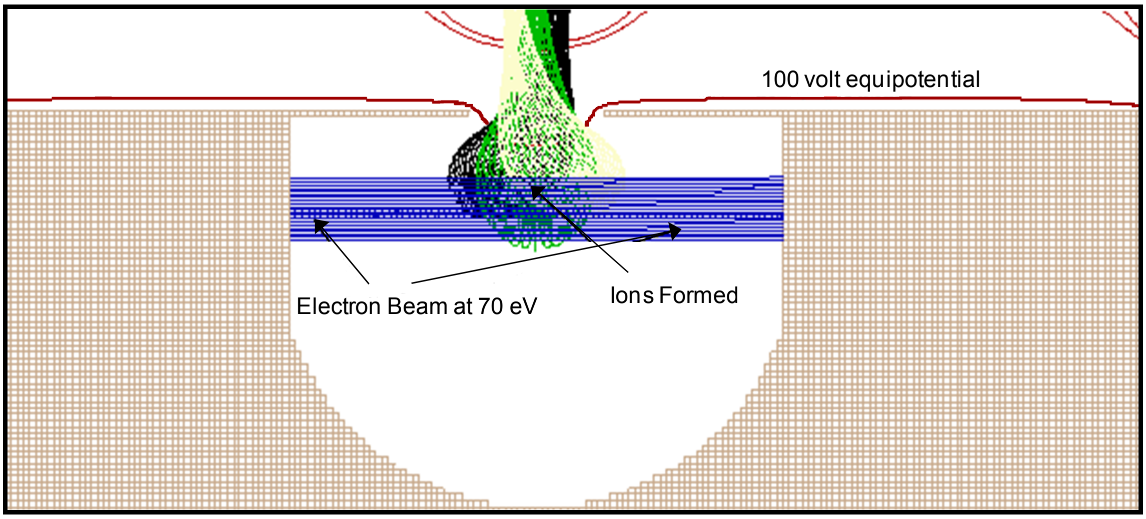


Figure S2: A schematic of the QUB TAP-1 system.

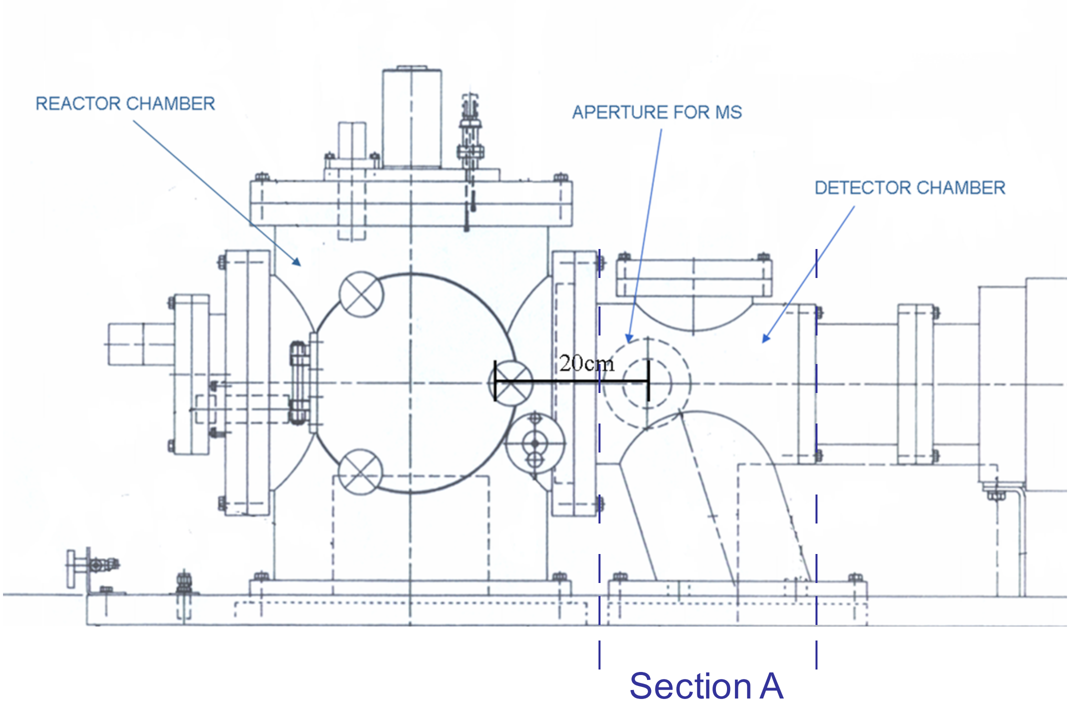


Figure S3: Plan view of Figure 4 Section A, the detector chamber.

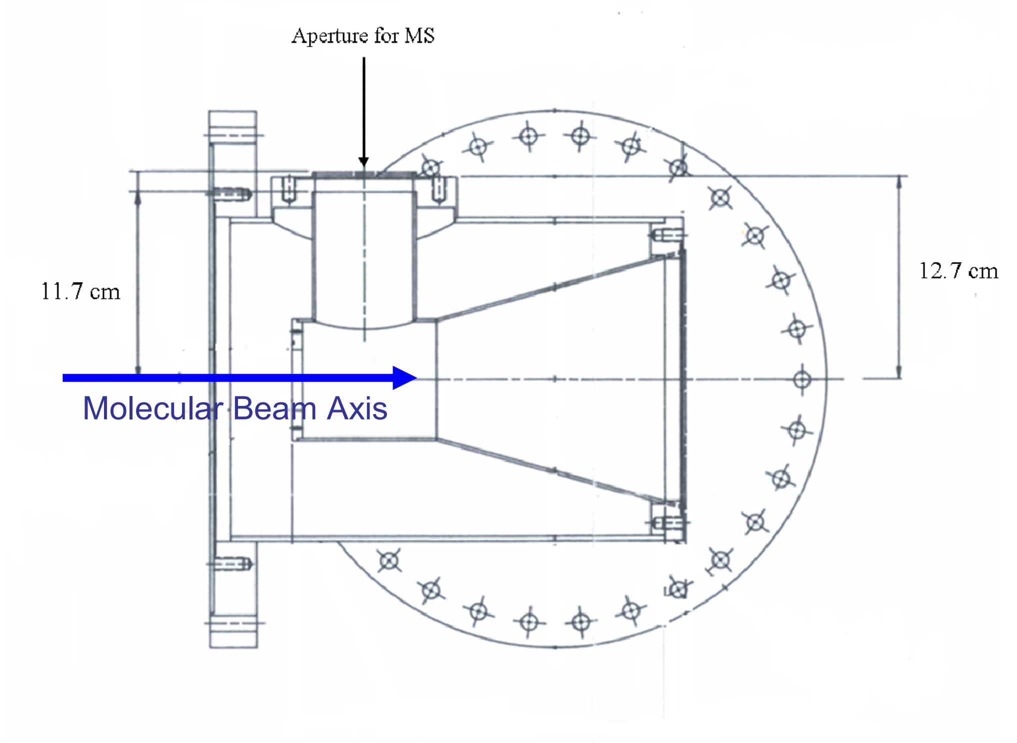


Figure S4: Schematic of the transfer optics system.

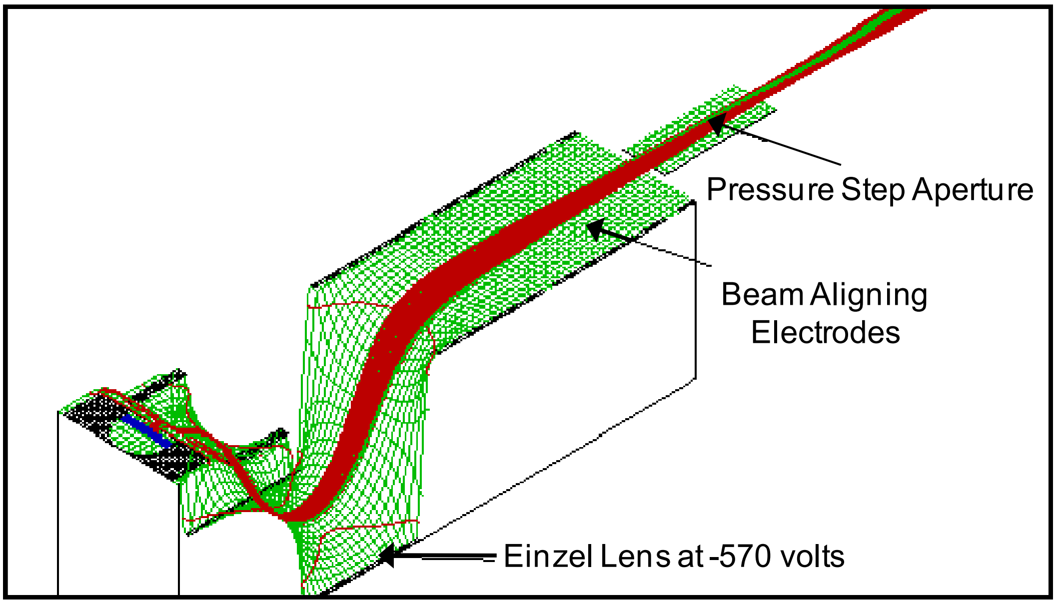


Figure S5: Schematic of the electrostatic analyzer (ESA).

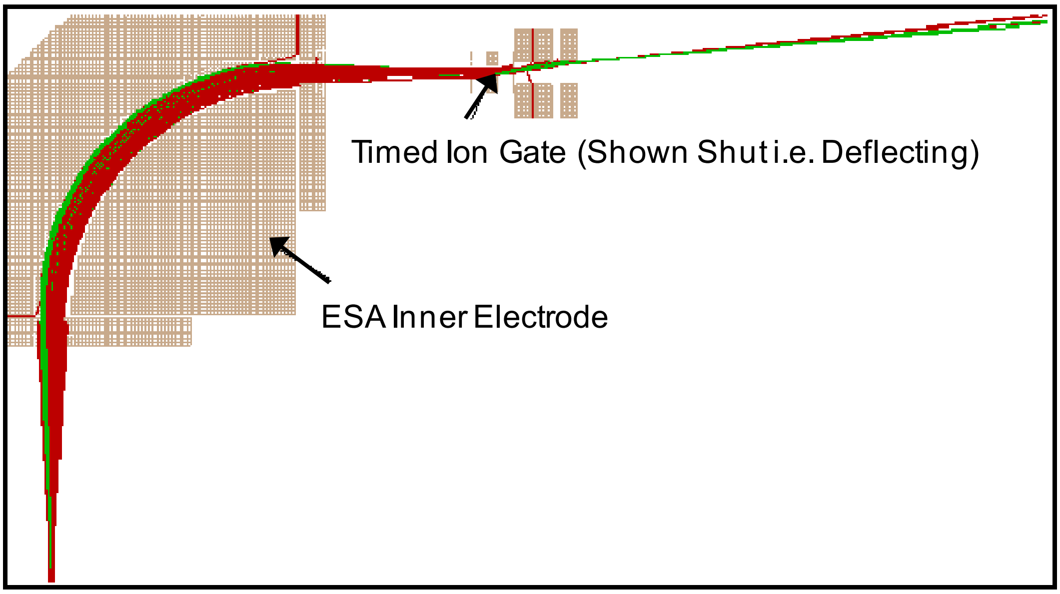


Figure S6: Schematic of the shaped field buncher.

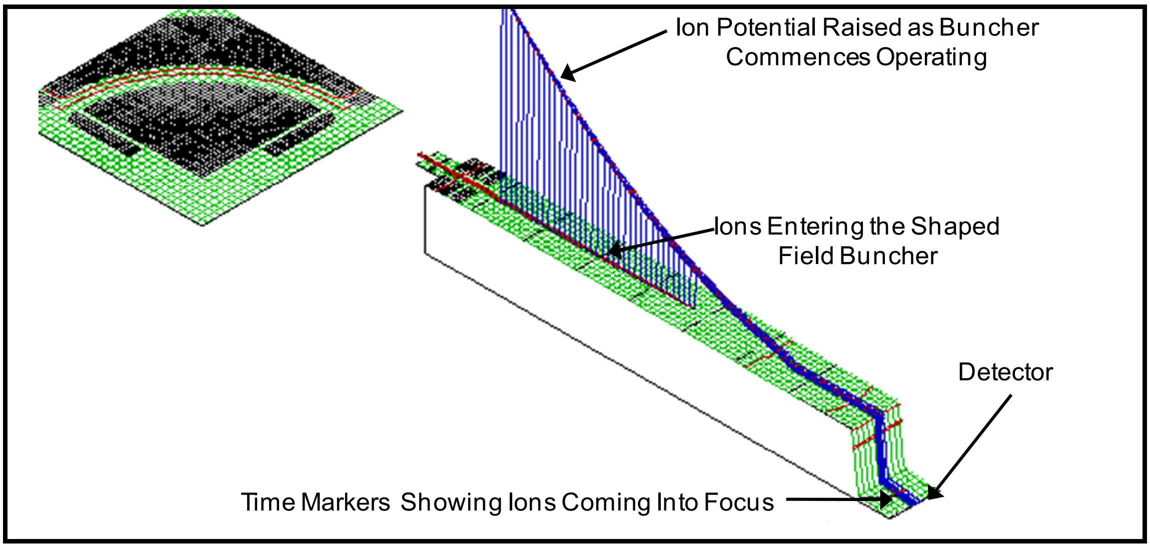
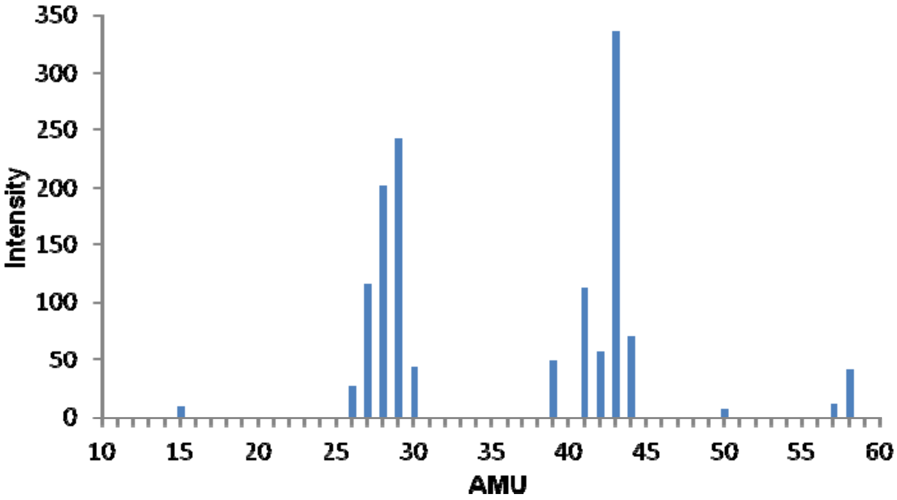


Figure S7: Mass spectrum of the hydrocarbon mix of butane, propane and ethane, recorded at 50 °C (baseline corrected).



Knudsen Diffusion TAP Theory

The corresponding one inert zone model of TAP experiment can be described by the Knudsen diffusion equation shown in Equation S1:

$$\varepsilon \frac{\partial C_g}{\partial t} = D \frac{\partial^2 C_g}{\partial x^2}$$

Equation S1

The TAP initial and boundary conditions do not depend on reactor packing but may depend on experimental setup and/or proper functioning of the system components (notably all pulsing and pumping devices). For properly working TAP-1 or TAP-2 systems, the conditions can usually be presented in the ideal form, demonstrated in Equations S2 to S4 [1]:

Zero initial condition:

$$C_g\Big|_{t=0} = 0$$

Equation S2

Narrow inlet pulse:

$$-A_r D \left.\frac{\partial C_g}{\partial x}\right|_{x=0} = 2N_g \delta(t)$$

Equation S3

Vacuum condition at the exit:

$$C_g\Big|_{x=L_r} = 0$$

Equation S4

The one-zone diffusional model can be solved using different methods (e.g. the method of separation of variables [2] or Laplace transformation [1]). Since no reaction is assumed, the area under the responses merely reproduces the pulse intensity. The following form of the area normalized solution for observed exit flow can be used to generate the diffusional response, as shown in Equation S5 [3]:

$$F_{exit}(t) = \frac{\pi}{2\tau_{res}} \sum_{n=0}^{\infty} (-1)^n (2n+1) Exp\left(-\frac{\pi^2 (n+\frac{1}{2})^2}{2\tau_{res}} t \right) \text{, where } \tau_{res} = \frac{\varepsilon L_r^2}{2D}$$

Equation S5

According to this expression (Equation S5), the diffusion response is determined by only one parameter, which can be used for fitting experimental curves. This parameter can be determined by calculating the first moment of the response, M_1, which gives the residence time in the reactor, as defined in Equation S6:

$$M_n = \int_0^{+\infty} t^n F_{exit}(t)dt \qquad \frac{M_1}{M_0} = \frac{\varepsilon L_r^2}{2D} = \tau_{res};$$

Equation S6

Besides fitting the response with the theoretical curve, other simple criteria for testing diffusion responses have been proposed:

1. The response shape should not depend on pulse intensity (area normalized response should be the same) [4]
2. The product of the peak height and peak time should be equal to 0.306 [3]
3. The modified second moment should be zero, as shown in Equation S7 [5]:

$$M_{2,mod} = \frac{M_2}{M_0} - \tfrac{5}{3}\left(\frac{M_1}{M_0}\right)^2 = 0$$

Equation S7

4. The residence time (first moment) should depend on temperature and molecular weight of the probe molecule according to the Knudsen diffusion theory for each inert TAP micro-reactor packing configuration, as is defined by Equation S8 [5]:

$$\tau_{res} \propto 1/D \propto \sqrt{M_w/T}$$

Equation S8

The fourth criterion justifies correct dependence of the observed responses on temperature and molecular weight which verifies the elimination of influences of fast physical adsorption, porous diffusion, etc.

In this work, criteria 1- 4 and curve fitting were applied to validate the TAP-ToF system.

Notation

A	variation range of detector efficiency
A_r	cross sectional area of the reactor (m^2)
B	gradient of slope
C	point of inflection
C_g	gas concentration (mol/m^3)
D	Knudsen diffusivity (cm^2/s)
F_{exit}	area-normalized exit flow (1/s)
$\vec{F}_{HC}^{raw}(t)$	exit flow vectors with 14 elements where each element is the raw (unnormalized) response observed for specific hydrocarbon at specific AMU (a.u./s)
$\vec{F}_{HC}^{n}(t)$	exit flow vectors with 14 elements where each element is the response of specific hydrocarbon at a specific AMU normalized to the argon intensity at AMU=40 assuming a 50/50 mix of hydrocarbon/Ar (a.u./s).
$f_{HC}(t)$	area normalized response corresponding to specific hydrocarbon.
I_{ab}	measured ion abundance
I_N	number of ions reaching the detector
L_r	length of the reactor (m)
M_n	moment of n^{th} order (mole*s^n)
M_w	molecular weight
N_g	pulse intensity (mol)
n_{HC}	composition coefficient for specific hydrocarbon.
t	time coordinate (s)
T	temperature (K)
x	space coordinate (m)
$\vec{X}_{HC}$	column vectors representing fragmentation pattern of specific hydrocarbon
$\hat{X}$	fragmentation matrix formed by column fragmentation vectors
τ_{res}	mean residence time (s)
ε	bed voidage

References

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