

# Fragmentation in cyclic traveling wave ion mobility cell

Faculty of Science

Karel Lemr<sup>1</sup>, Štěpán Dostál<sup>2</sup>, František Tureček<sup>3</sup>, Karel Lemr<sup>2</sup>

karel.lemr@upol.cz

<sup>1</sup>Joint Laboratory of Optics of Palacký Univ. and Institute of Physics AS CR, Faculty of Science, Palacký University

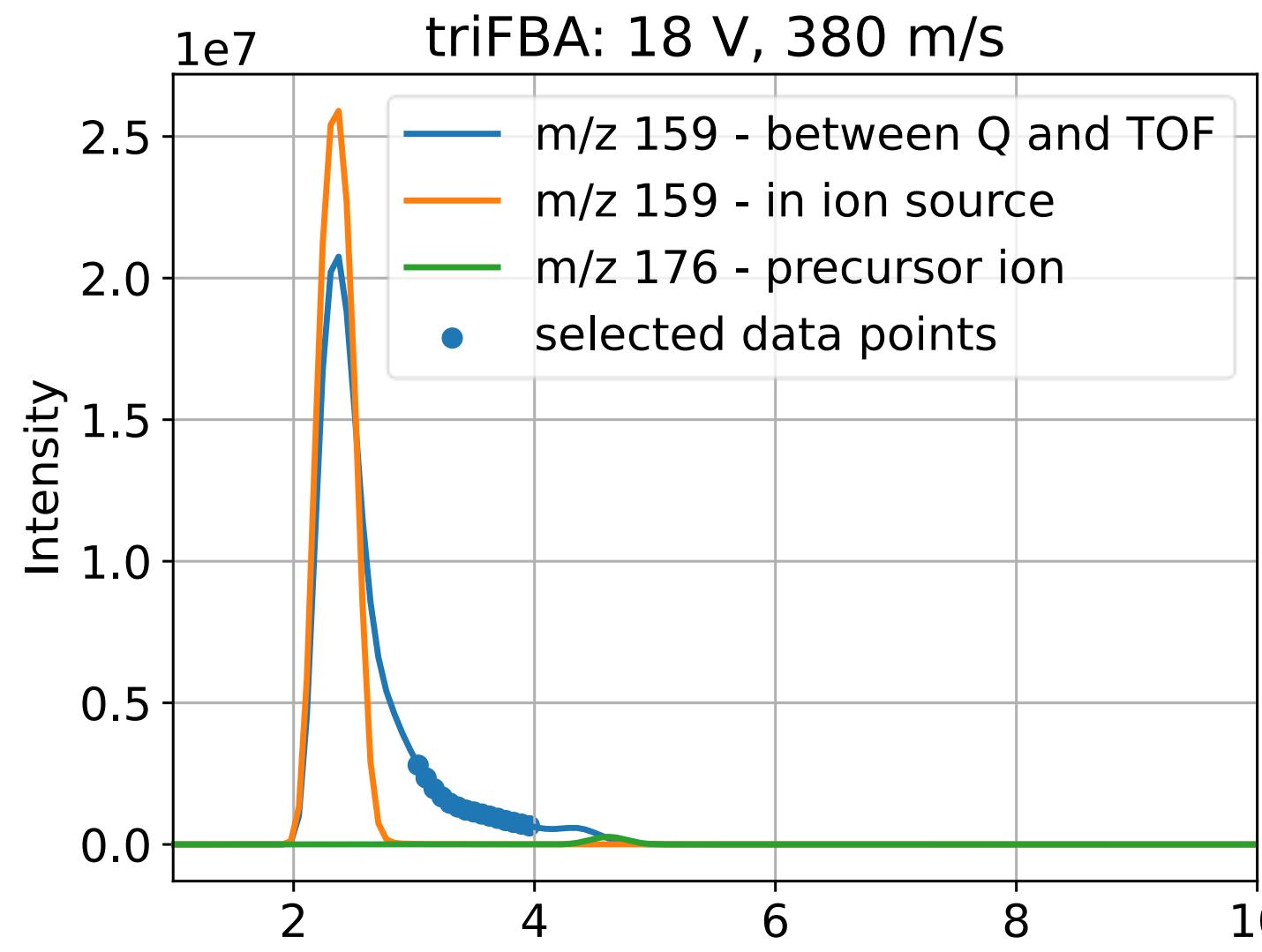
<sup>2</sup>Dept. of Analytical Chemistry, Faculty of Science, Palacký University, 17. listopadu 12, Olomouc 779 00, Czech Republic

<sup>3</sup>Department of Chemistry, University of Washington, Seattle, Washington 98195-1700, United States

## 1 Introduction

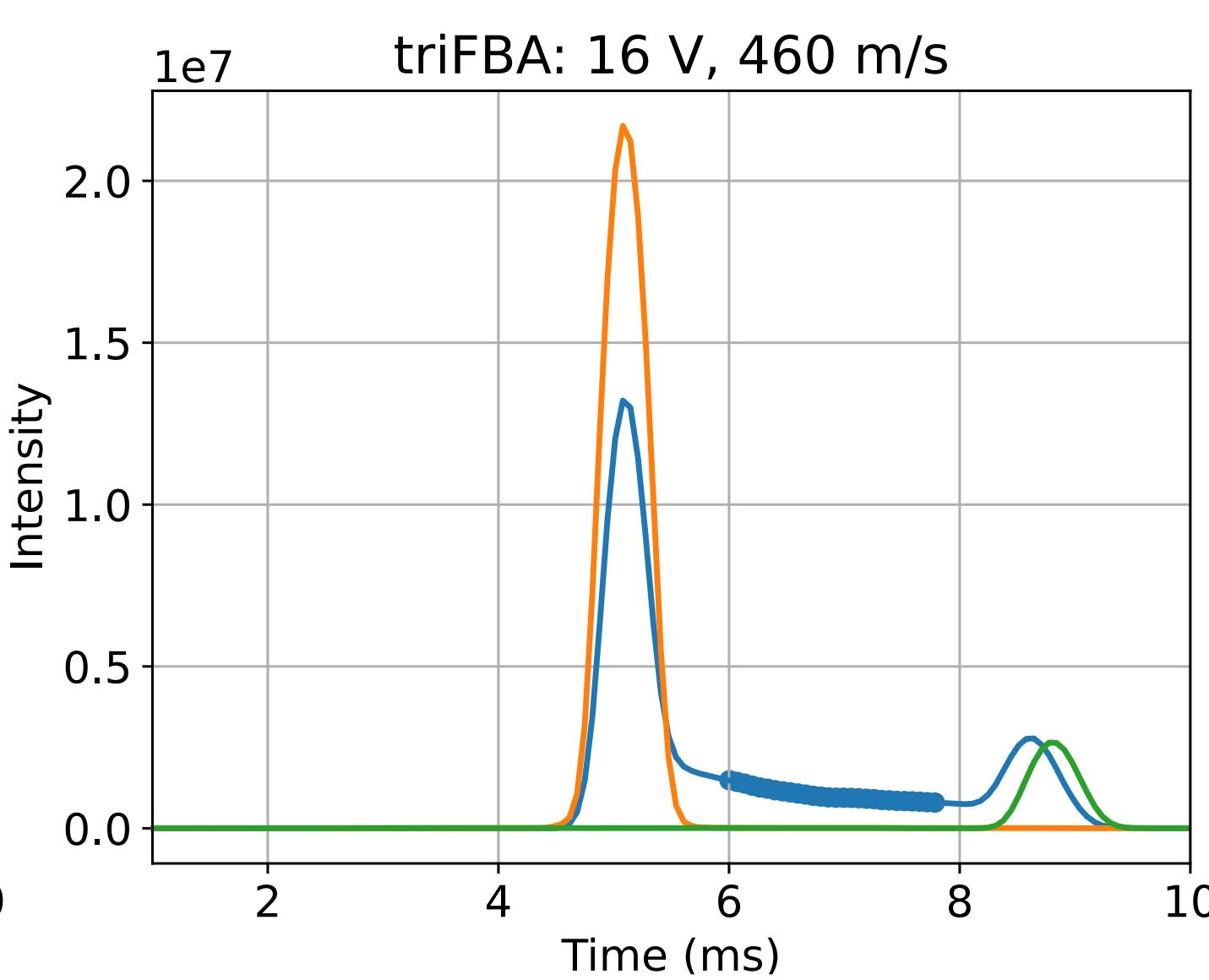
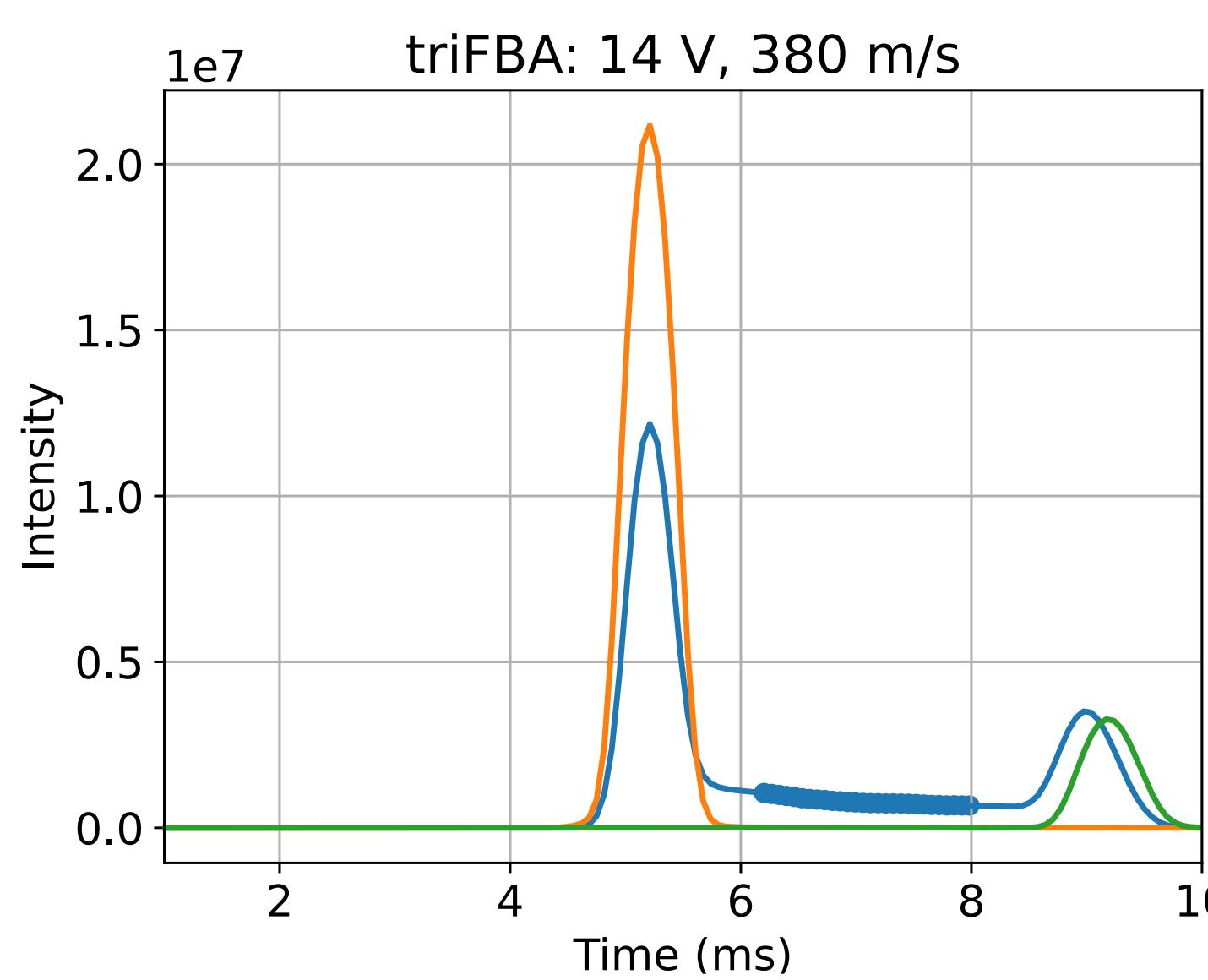
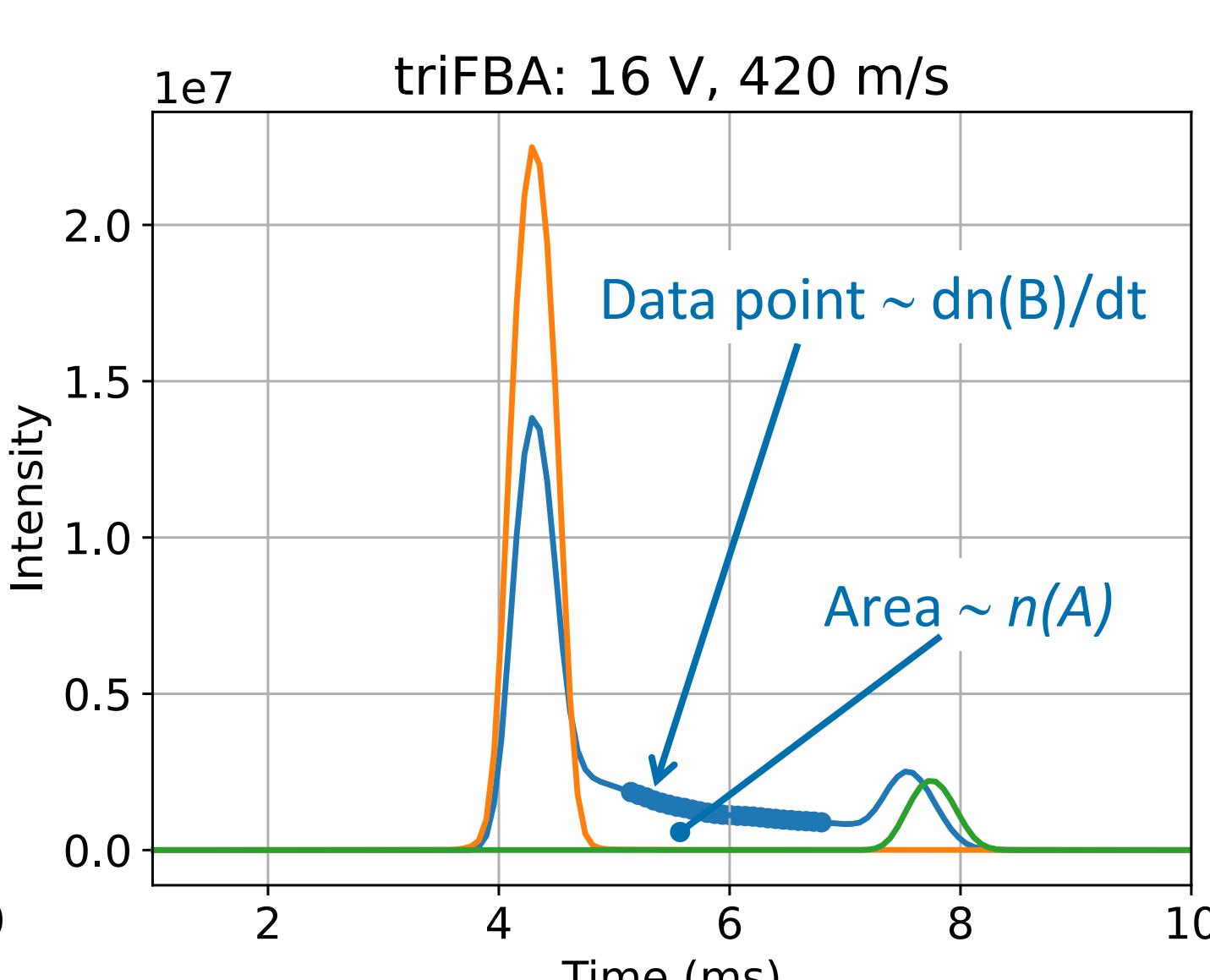
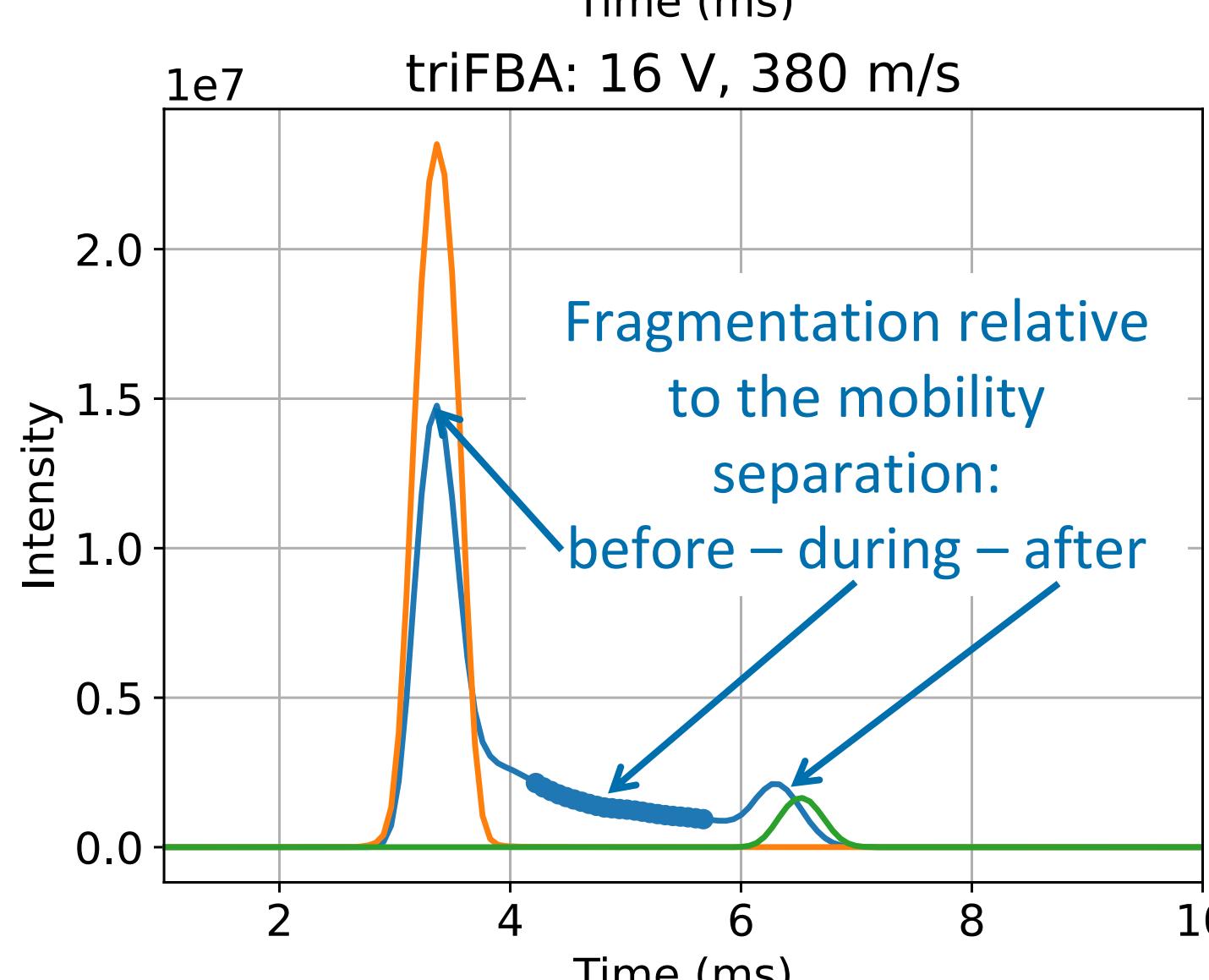
Coupling ion mobility to mass spectrometry improves the differentiation of isomers.[1] Increasing the resolving power of ion mobility can enhance isomer separation; however, arrival time distribution (ATD) profiles can also be used to determine isomeric ratios, even for strongly overlapped peaks.[2] ATD profiles are affected by ion fragmentation. For linear traveling wave ion mobility, the effect of separation parameters on the effective temperature ( $T_{\text{eff}}$ ) inside the cell was studied.[3-5] Here, we focus on ion fragmentation in cyclic ion mobility by determining the rate constant changes in the cell.

## 3 Results



**Fig. 1:** Fragmentation of triFBA ( $A^+$ , m/z 176) to fragment ion  $B^+$  (m/z 159, the loss of ammonia) under different setting of traveling wave height (18, 16 and 14 V) and velocity (380, 420 and 460 m/s). Selected data points are not influenced by fragmentation before and after mobility separation.

Higher wave, lower velocity – higher ion energy.



**Tab. 2:** k-values determined using: procedure 1 - integration of mobilograms, k-value for the last selected data point (see Fig. 1); procedure 3 - integration of k(t), k-value at the time of the first selected data point + 5 ms.

Ion	Wave height (V)	Wave vel. (m/s)	1	Taylor polynomial order		
				1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>
triFBA	18	380	1.43	1.13	1.16	1.17
		420	0.87	0.78	0.80	0.81
		460	0.64	0.56	0.58	0.59
	16	380	0.44	0.39	0.40	0.41
		420	0.31	0.22	0.26	0.27
		460	0.23	0.13	0.19	0.19
	14	380	0.15	0.09	0.12	0.13
		380	0.38	0.40	0.43	0.43
MeOBP	16	380				

## 2 Experimental

- SELECT SERIES Cyclic IMS QTOF (Waters, U.K.) - cyclic traveling wave ion mobility, electrospray, positive mode, direct infusion (5  $\mu$ L/min)
- The effect of cyclic ion mobility settings was investigated by fragmenting thermometer ions[6]:  
4-(trifluoromethyl)benzylammonium (triFBA, dissociation energy 1.89 eV)  
4-methoxybenzylpyridinium (MeOBP, 1.84 eV)  
4-methylbenzylpyridinium (MeBP, 2.27 eV)
- The model fitting and the integration were coded in Python

## Rate constant evaluation – three procedures

$$dn(B)/dt = k \cdot n(A)$$

n - amount of substance, t - time

Each data point in the middle segment represents  $dn(B)/dt$  (Fig. 1), but the rate constant k varies during ion mobility separation due to heating/cooling processes.

Model derivation

Arrhenius equation:  $k(T) = A \cdot \exp(-E_a/k_B T)$   
 $E_a$  - activation energy,  $k_B$  - Boltzmann constant, T - absolute temperature

n(A) – integration of mobilogram, k determined for each selected data point (see Fig. 1)

Taylor polynomial of k(T)

Newton's law of cooling:

$T(t) = (T_1 - T_2) \exp(-\gamma t) + T_2$   
 $T_1$  - initial temperature,  $T_2$  - surrounding temperature

The zero-order Taylor polynomial cannot be used for fitting (p-value = 0, see Tab. 1)  $\Rightarrow$  k is not constant in time.

derived k(t) function – the best fit to a series of k-values from 1

introduction of k(t)  $\Rightarrow$  K(t)  
K(t) - the best fit to selected data points (see Fig. 1)

**Tab. 1:** Data curve fitting using different orders of the Taylor polynomial (selected data points, Fig. 1).

Wave height (V)	Wave vel. (m/s)	0 <sup>th</sup>	Taylor polynomial order		
			1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>
18	380	Red. X <sup>2</sup>	17.07	1.251	0.7356
		p-value	0.0000	0.2582	0.6766
16	380	Red. X <sup>2</sup>	6.250	0.3821	0.3162
		p-value	0.0000	0.9892	0.9965

## 4 Conclusion

- Procedures (1) and (3) were comparable (Tab. 2), (2) showed inconsistencies in extrapolated k-values for the 2<sup>nd</sup> and 3<sup>rd</sup>-order Taylor polynomials.
- Due to the effect of dynamic conditions in the ion mobility cell, k-values should not be considered absolute. However, they do reveal the relative effect of the experimental parameters.
- For triFBA, extrapolation to a steady state confirmed: the k-values increased with higher wave height, but decreased with higher wave vel., e.g., for Tab. 2 (3, 2<sup>nd</sup>), 380 m/s:  $k(18 \text{ V})/k(16 \text{ V}) = 2.9$ ; 16 V:  $k(420 \text{ m/s})/k(380 \text{ m/s}) = 0.65$ .
- The k-values were similar for MeOBP and triFBA (Tab. 2), but significantly lower for MeBP (k<0.1). This was consistent with their dissociation energies. The trends observed corresponded to the changes found for  $T_{\text{eff}}$  [3-5], but our approach allows k-value changes to be followed over ion mobility separation and extrapolated to steady state.

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