# Modelling space charge effects in Transversal Modulation Ion Mobility Spectrometry

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SEADM

César Barrios-Collado[a,b], Guillermo Vidal-de-Miguel[c,*]

[a]SEADM S.L., [b]University of Valladolid, [c]Fossil Ion Technology

*guillermo.vidal@fossiliontech.com

## 1. Overview

- Transversal Modulation Ion Mobility Spectrometry (TMIMS) [1,2] provides a continuous beam of selected ions, add-on architecture which can be coupled easily to pre-existent Mass Spectrometers, and even other TMIMS to provide IMS-IMS pre-filtration.
- Earlier modeling efforts [3] have been focused on the optimization of the geometry.
- The transmission through TMIMS is limited mainly by space charge effects. However, these aspects are still not quantitatively analyzed, in part due to the lack of appropriate numerical tools.
- In this work we have studied the effect of space charge. For this purpose, we have:
  - Created of an specific numerical tool.
  - Studied the behavior of the main performance variables (frequency of resonance, maximum peak signal and resolving power.

## 2. Hypotheses

- The composition of ion mixture in TMIMS is usually dominated by low molecular weigh ions, with small cross section and high mobility.
- Analytes are usually heavy compounds (e. g. proteins [4,5]) with lower mobility.
- In our model, we consider two species: a buffer ion with mobility $Z_b$ which is in high concentration, and a target ion, with mobility $Z_t$ which is in very low concentration. $Z_b > Z_t$.
- Concentration of target ion is low enough to consider its space charge effects negligible.
- The space charge effect of the buffer ion beam over the target ion beam is introduced as a perturbation superposed over the electric fields caused by electrodes.
- For convenience the space charge effect of the buffer ion beam over itself is not considered.

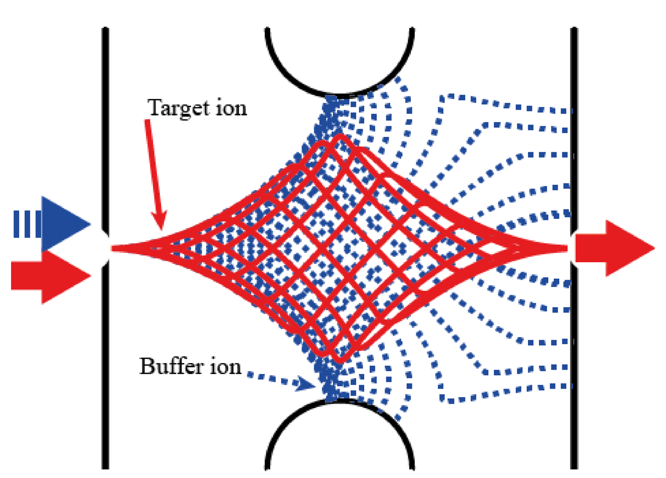


*Figure 1. Representation of trajectories of target (red) and buffer (blue) ions.*

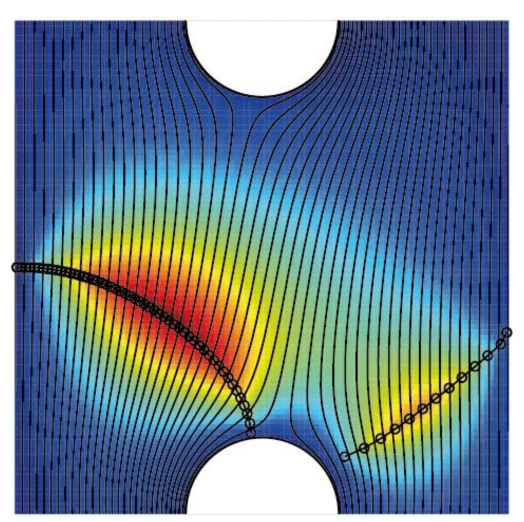

*Figure 2. Buffer beam. Black lines are voltage without space charge; color regions are the perturbation.*

## 3. Degradation of spectra

- The algorithm sweeps the mobility ratio $Z_b/Z_t$ and the dimensionless ionic current $I/I_{ref}$. Ionic current, $I$, is scaled with $I_{ref}$ which is defined as the buffer ionic current whose space charge perturbation over the target ion trajectories is in the same order of TMIMS convective displacements. It is estimated as follows:
  - The electric field caused by space charge is in the order of $E_{sc} \sim nel/\varepsilon_0$, where $ne$, $\varepsilon_0$ and $l$ are the beam charge density, the vacuum permittivity and the TMIMS length respectively.
  - The time of residence of a target ion in TMIMS is in the order of $t_r \sim l^2/Z_t/V_0$, where $V_0$ is, the axial voltage.
  - Then, the total displacement caused by space charge is in the order of $\sim Z_t E_{sc} t_r = nel^3/(V_0\varepsilon_0)$.
  - So, the buffer beam charge density when this displacement is in the order of the convective path ($l$) is: $ne \sim V_0\varepsilon_0/l^2$
  - This corresponds to a ionic current of: $I_{ref} = qV_0\varepsilon_0/l^2$, where $q$ is the volumetric flow.
- At $Z_b/Z_t < 1.2$ the algorithm seems to be unstable, regardless of the ion current, mainly due mathematical singularities.
- As expected, space charge effects have a negative effect on TMIMS performance.

- At a fixed $Z_b/Z_t$ the frequency of resonance shifts, and the spectra shape degrades as $I/I_{ref}$ is increased.
- Too high $I/I_{ref}$ degrades spectra to unrecognizable shapes (so there is a maximum $I/I_{ref}$ TMIMS can handle, which depends on $Z_b/Z_t$).
- This maximum $I/I_{ref}$ increases with $Z_b/Z_t$.
- At very high $Z_b/Z_t$ spectra is not degraded.

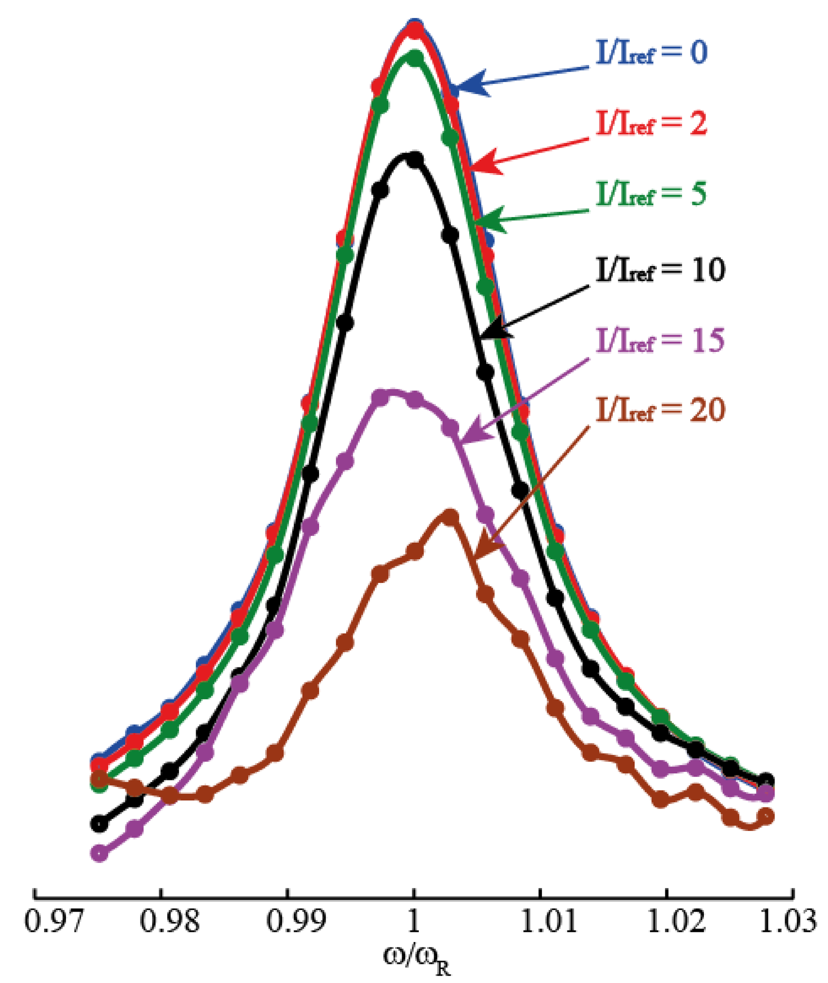


*Figure 3. Degradation of spectra ($Z_b/Z_t$ = 1.25).*

## 4. Effects on performance

Figure 4 shows the changes of the main performance parameters (referenced to their value at the no space charge case) for different $I/I_{ref}$ and $Z_b/Z_t$:

- Resonant frequency ($\omega_R$) shifts linearly with $I/I_{ref}$ at a fixed $Z_b/Z_t$.
- Peak signal, $S$, (signal at resonant frequency) drops quadratically (without linear component) with $I/I_{ref}$ at a fixed $Z_b/Z_t$.
- Resolving power, $R$, was fit to a cubic trend (without linear component) with $I/I_{ref}$ at a fixed $Z_b/Z_t$.
- $\omega_R$, $S$ and $R$ follow rational functions of $Z_b/Z_t$ when $I/I_{ref}$ is constant.

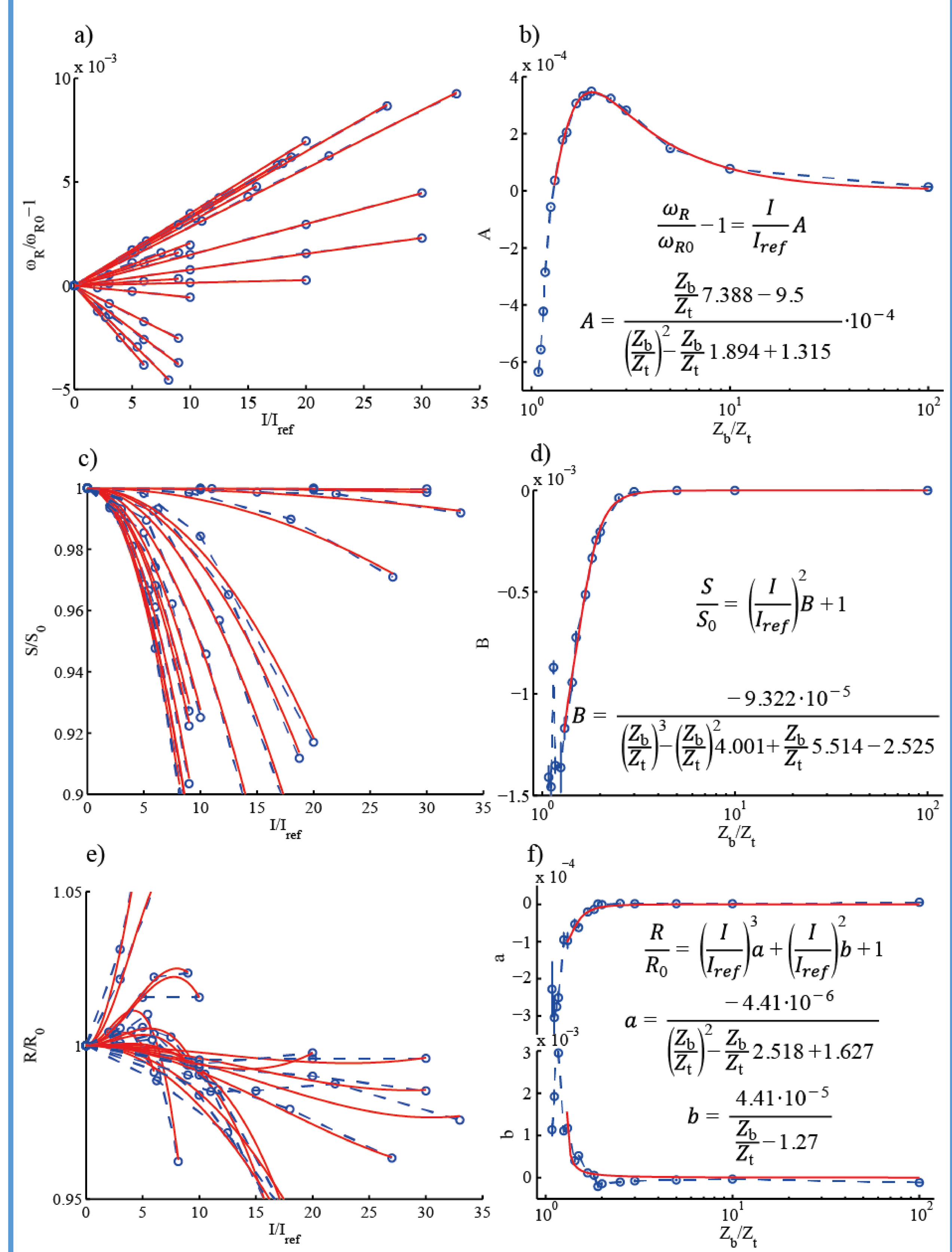


*Figure 4. Changes in performance for different $I/I_{ref}$ and $Z_b/Z_t$: a),b) resonant frequency; c), d) peak signal; e), f) resolving power.*

## 5. Concluding remarks

- Our numerical method showed signs of instability when the mobility ratio tended to be unitary (regardless the ion current), mainly due to mathematical singularities. However, when the mobility of the buffer ion is a 20% higher than the target ion, and onwards, the algorithm behaves robust, which covers the expected range of mobilities in real experiments.
- According to the results provided by our method, we conclude that space charge effects produce a general loss of performance on TMIMS devices, displacing the frequency of resonance and lowering transmission and resolving power. This is a consequence of the undesired deviations on the convective paths of the target ions caused by the buffer ion beam space charge electric field.
- In the worst-case scenario, the maximum ionic current which can be handled by the TMIMS is:
  - $I/I_{ref} \sim 10$ at $Z_b/Z_t \sim 1.2$.
  - For a TMIMS with $V_0 = 8\ kV$, $l = 5\ cm$ and $q = 1\ lpm$ it results on $I \sim 5\ nA$.

## 6. Acknowledgements

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## 7. References

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