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Retrieval of time resolved ion mobility from phase dependent modulated compensation voltage in Differential Ion Mobility Spectrometry

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Introduction

Differential ion mobility spectrometry uses the field dependent mobility of chemical species to separate them in an alternating asymmetric high voltage (*separation voltage*, SV). The SV causes a radial diversion of ions in their axial trajectory. To compensate this diversion, a second voltage, the *compensation voltage* (CV), is applied. In common DMS devices this voltage is used as a DC. We present the effects of a modulated CV on the ions in the DMS cell and attempts to retrieve the time resolved ion mobility from simulated DMS experiments with phase-shifted modulated CV.

Simulation

The simulation of an DMS experiment with modulated CV is part of the Ion Dynamics Simulation Framework (IDSimF) [1]. The simulation calculates the reaction kinetics and radial transport of proton bound water clusters (R1) as a model system. The SV and CV can be arbitrary functions with a variable phase shift.

The optimal CV amplitude is fond in an iterative process, minimizing the motion of the ion ensemble in the separation axis.

$$[H + (H_2O)_n]^+ + H_2O + N_2 \rightleftharpoons [H + (H_2O)_{n+1}]^+ + N_2 \qquad (R1)$$
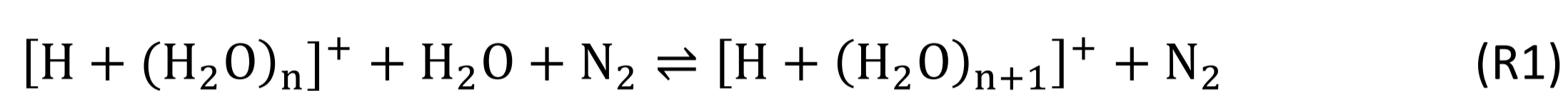
Methods

The diversion of ions in the DMS drift tube is a consequence of the field dependent differential mobility in the asymmetric SV field. Commonly, a DC voltage is applied as CV to compensate the diversion.

Due to the SV field, the ion mobility is also a *time dependent periodic* function.

Now, we use a CV modulated by a "*kernel function*" (e.g., a 50%-square kernel, Fig. 1), which causes the CV to be 'active' over only a certain period in an SV oscillation. The correction of the ion diversion by the CV takes place with the actual ion mobility of the ions which depends on the SV waveform. If the CV acts in a high field phase, the mobility is high and vice versa (Fig. 2). Thus, the optimal CV value becomes phase dependent on the SV (Fig. 3).

This phase plot contains information about the periodic, time resolved ion mobility.
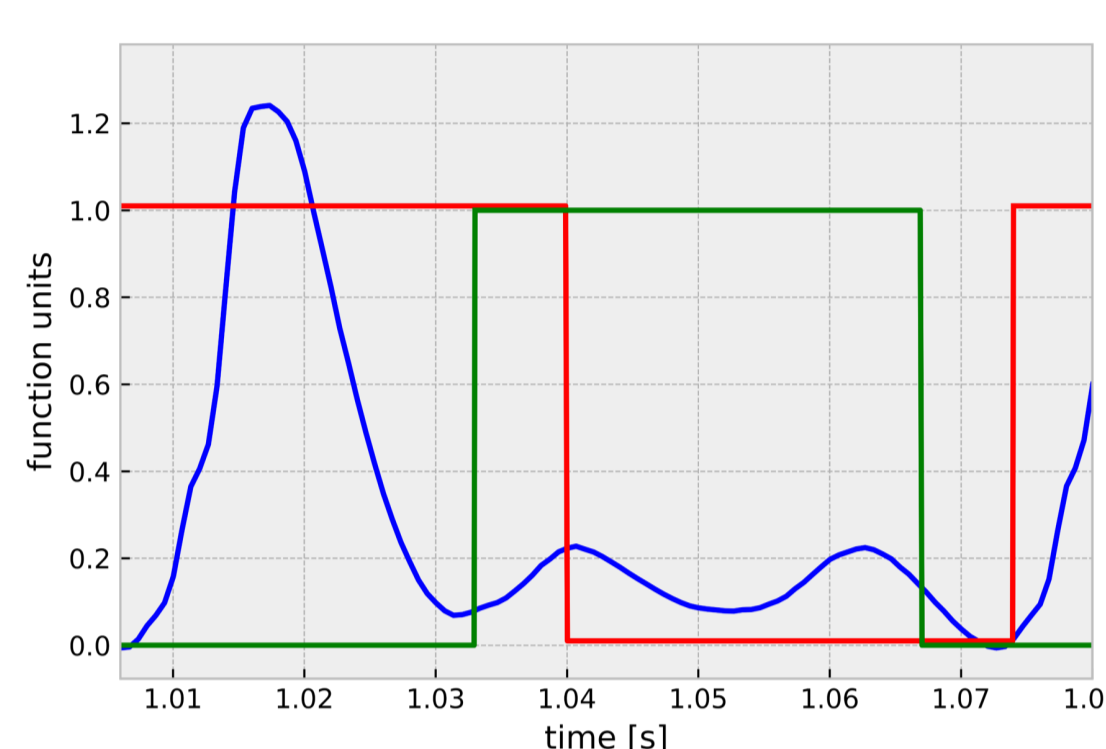

Figure 1 (above): Ideal 50%-Square kernel function, which essentially switches the CV either on and off for an equal same amount of time.

Figure 2 (left): Schematic of the applied phase shift with a 50%-Square kernel function and the time dependent mobility induced by a bisinusoidal SV (blue). The red function is defined with a phase shift of 0. The green function has a phase shift of 0.4.

Figure 3 (right): Optimal CV amplitudes in dependence of phase shift between a bisinusoidal SV and a modulated CV (50% square kernel). The CV values are strongly dependent on the phase shift and contain information about the dynamics of the ion ensemble.
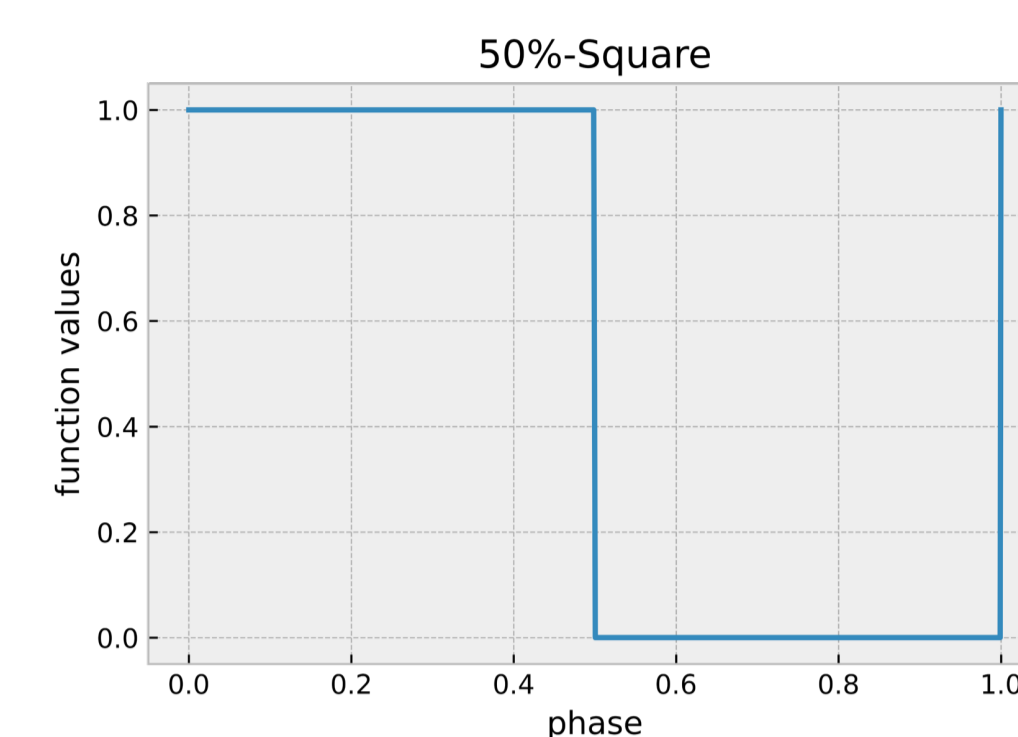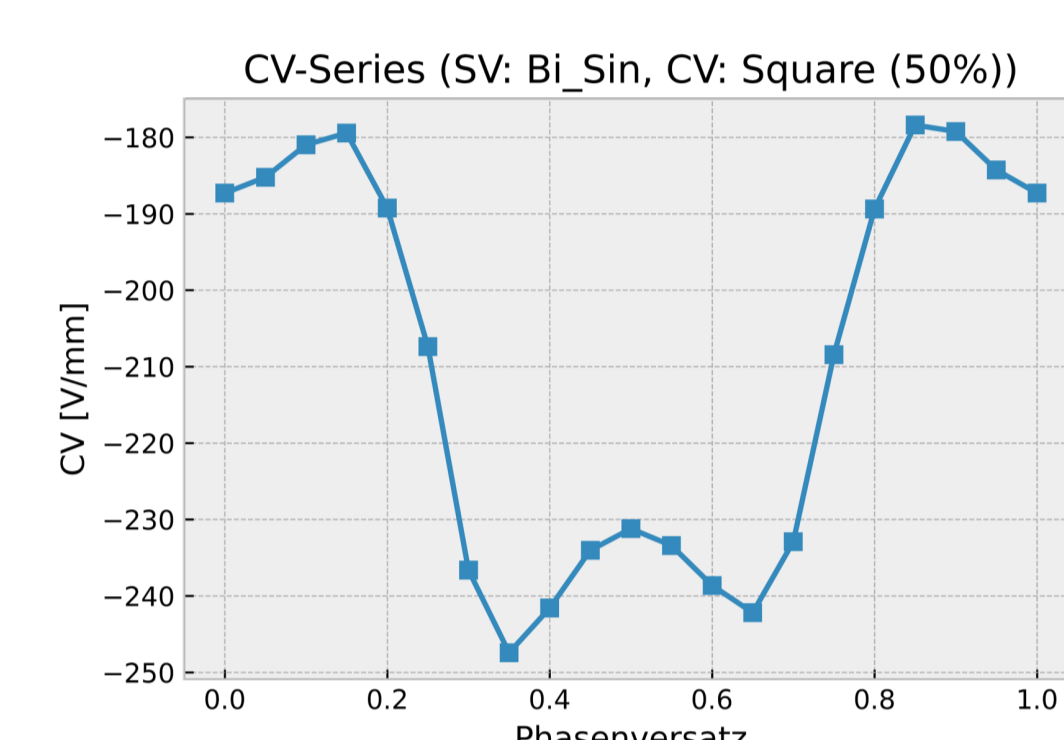

Effects of modulated CV on ion ensemble

The modulated compensation voltage creates various effects on the simulated ion ensemble. The clustered ions as the simulated proton-water-cluster system (R1) dissociate in high-field conditions and have thus a higher mobility as in low-field. For such clustered systems, the ion mobility is directly dependent on the SV amplitude. As shown in the graphics below (Fig. 4) the time resolved ion mobility closely resembles the applied SV waveform if no modulated CV is applied.

With a modulated CV, the ion mobility is dependent on the *combined* electric field of SV and modulated CV. The dependence on the voltage strength is shown in Fig. 5 with increasing voltages from 0 V to -300 V. The deviation created by the CV increases linear. The effects by phase dependence are shown in Fig. 6 with a 10%-Square kernel as modulated CV and variating phase shifts from 0 to 0.8. Here it is noted, the deviation created by the modulated CV moves within the SV period in dependence of the defined phase shifts.
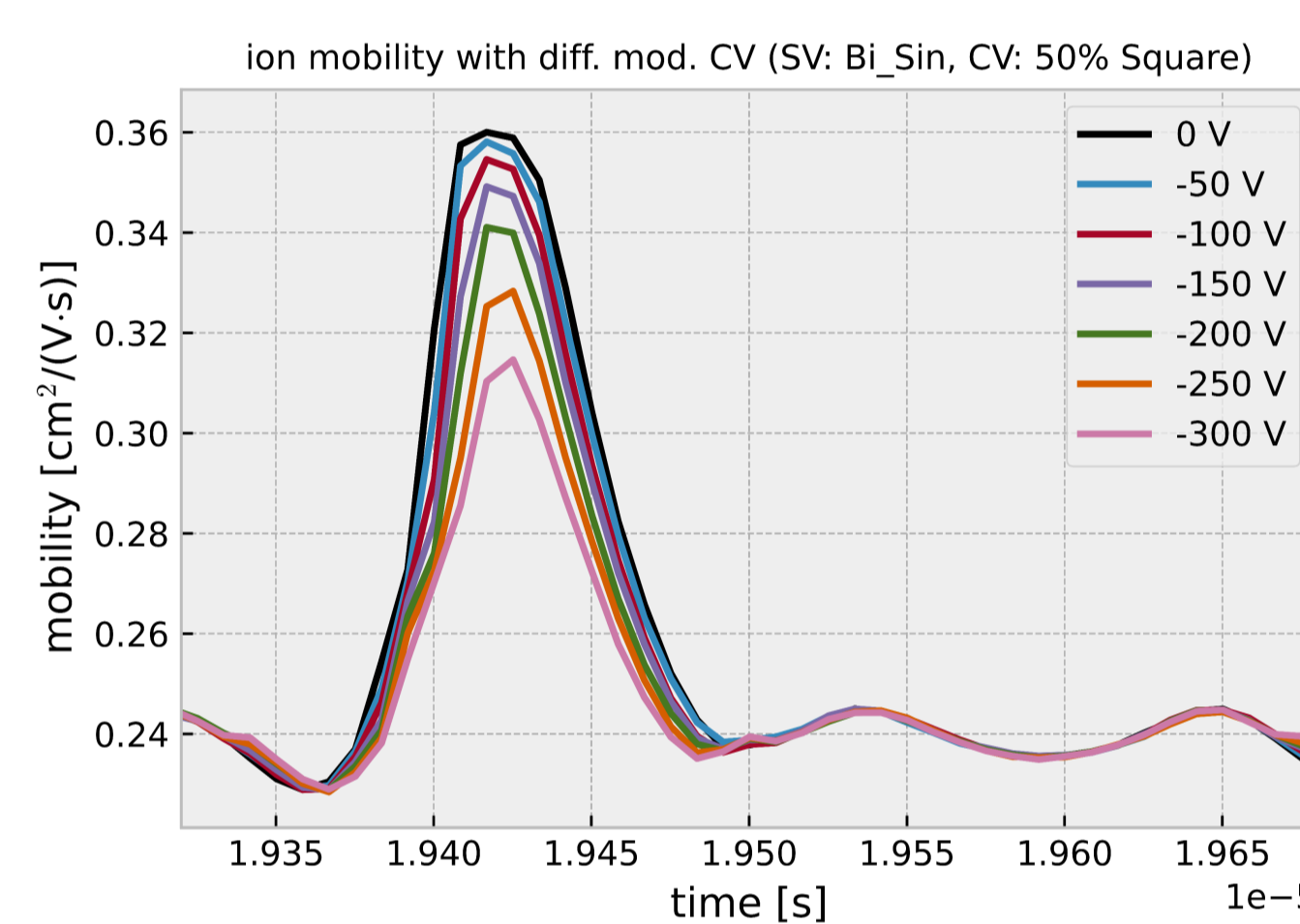

Figure 5 (left): Effect of CV amplitude on the ion mobility with 3000 V SV field strength and an 50% square CV with a phase shift of 0.0. The deviation of the mobility increases with the applied voltage.

Figure 4 (left): The ideal time resolved ion mobility is defined as the ion mobility without the effects of a modulated CV. The panels show the simulations with a bisinusoidal SV (left) and a square SV (right).
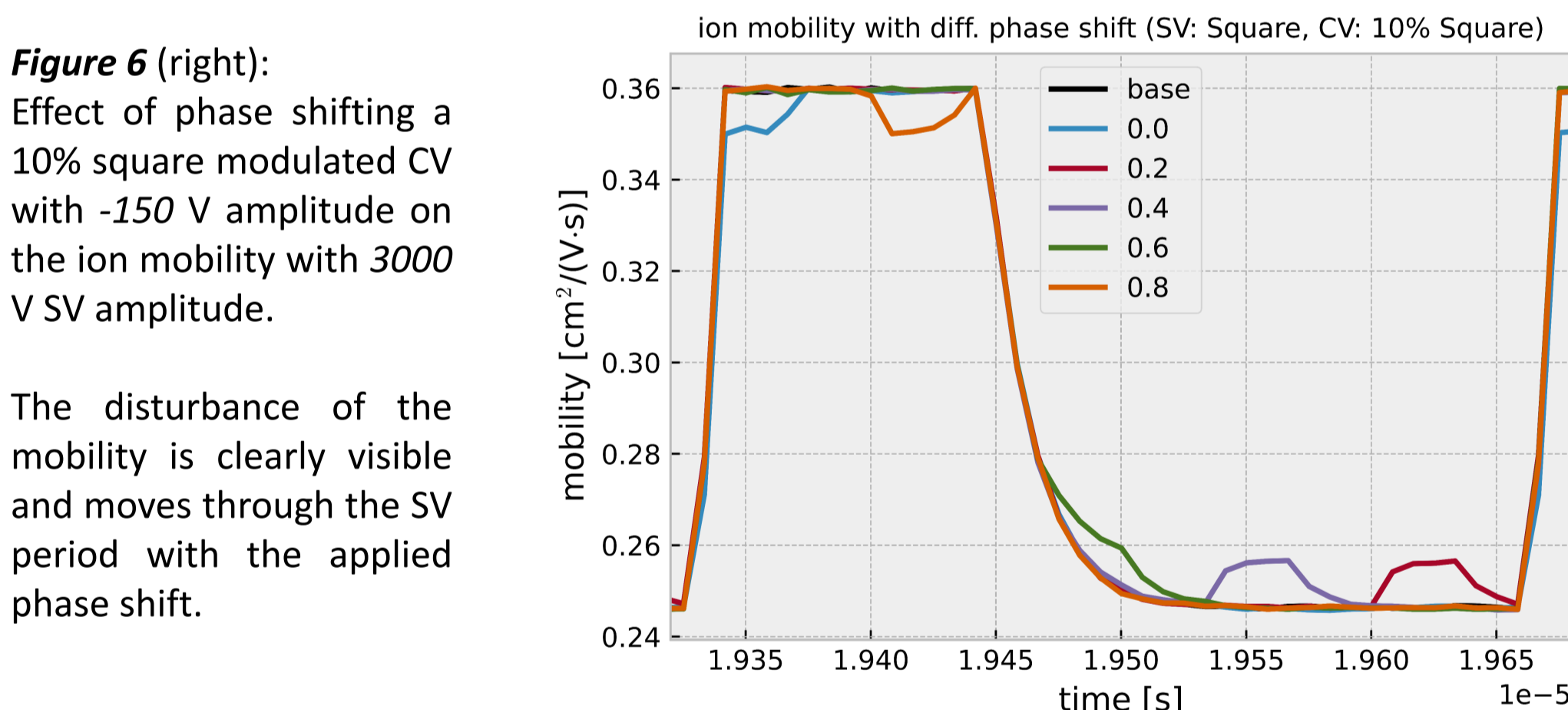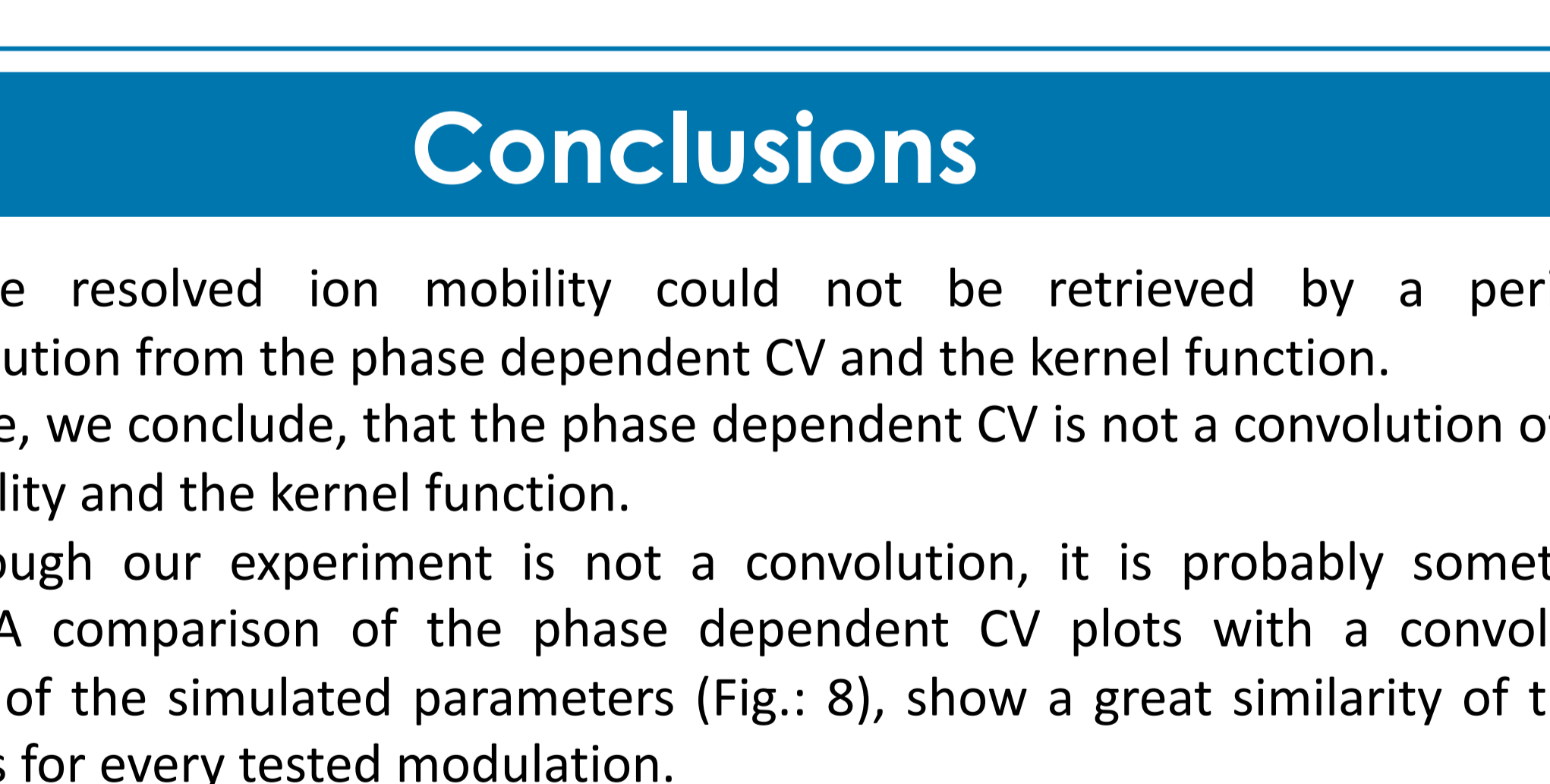
Figure 6 (right): Effect of phase shifting a 10% square modulated CV with *-150* V amplitude on the ion mobility with *3000* V SV amplitude.

The disturbance of the mobility is clearly visible and moves through the SV period with the applied phase shift.

Deconvolution of phase dependent CV

It was assumed that the periodic phase dependent CV plot (Fig. 3) is a convoluted function of the time resolved ion mobility (Fig. 4) and the CV kernel function. Therefore, to retrieve the time resolved ion mobility, a deconvolution of the phase dependent CV plots with the kernel function was attempted. Figure 7 shows the approach of the periodic deconvolution for a simulation with a square SV waveform and a triangle kernel function, based on a Fourier-transformation. The result shown in 'Retrieved Mobility' has no similarity to the Original Ion Mobility in the right panel of Fig. 7, despite the very high agreement of the input and minimized Phase - CV functions.
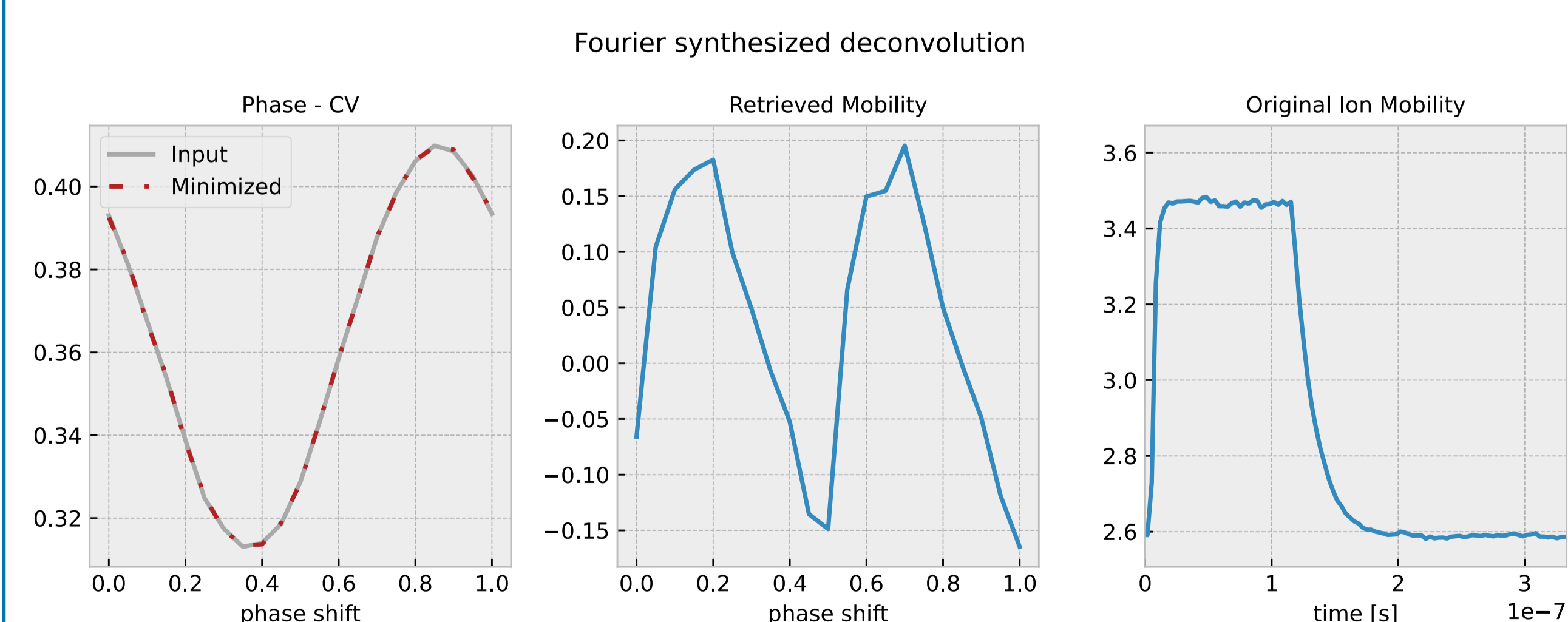

Figure 7 (left): Results of a periodic deconvolution for phase dependent CV ('Input', left panel) with a triangle kernel. The deconvoluted signal ('Retrieved Mobility', center panel) shows no similarity with the original time resolved ion-mobility (right panel) despite the very high agreement between minimized and input Phase – CV funtions.

Conclusions

- The time resolved ion mobility could not be retrieved by a periodic deconvolution from the phase dependent CV and the kernel function.
- Therefore, we conclude, that the phase dependent CV is not a convolution of the ion mobility and the kernel function.
- Even though our experiment is not a convolution, it is probably something similar: A comparison of the phase dependent CV plots with a convoluted function of the simulated parameters (Fig. 8), show a great similarity of these functions for every tested modulation.
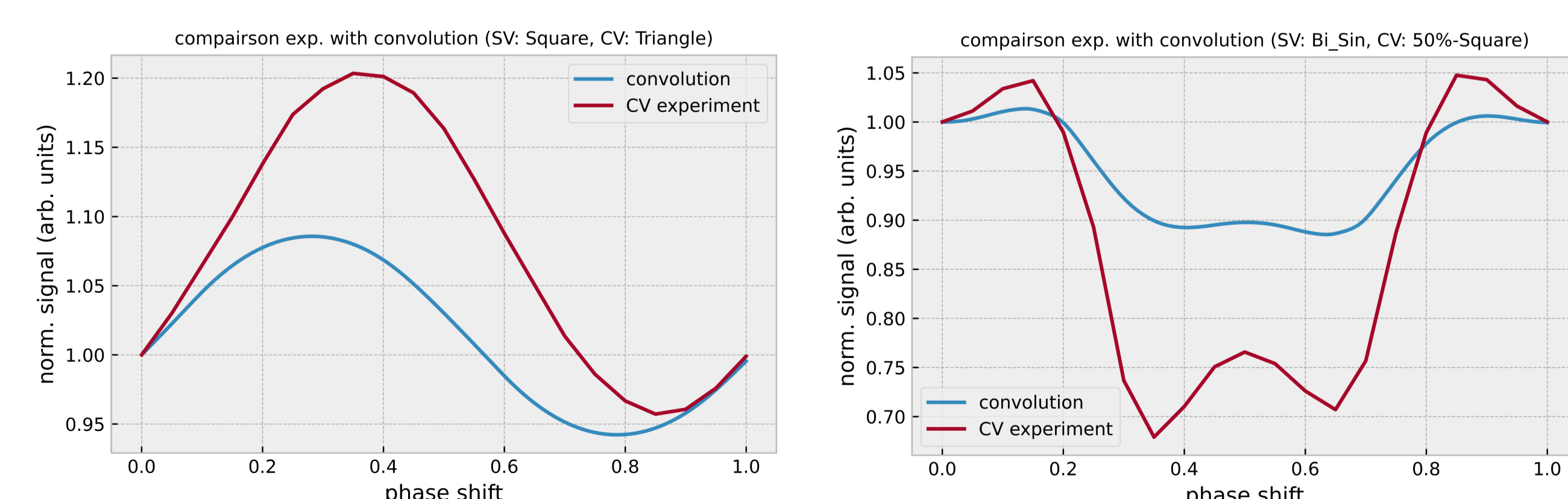

Figure 8 (above): A comparison of the phase dependent CV plots (red) and the convolved function (blue) of the time resolved ion mobility with the kernel function shows a great similarity in every simulation. The two plots above show this for two variations.

Acknowledgment

References

[1]   Wissdorf, W.; Erdogdu, D.; Thinius, M.; Benter, T.; *Ion Dynamics Simulation Framework (IDSimF) An open source trajectory simulation framework.* In: Proceedings of the 68th ASMS Conference on Mass Spectrometry and Allied Topics, virtual (2020)

[2]   Schneider, B.B.; Nazarov, E.G.; Londry, F.; Vouros, P.; Covey, T.R.: *Differential mobility spectrometry/mass spectrometry history, theory, design optimization, simulations and applications.* Mass Spectrom. Reviews 35, 687-737 (2016)