Prediction of ion mobilities using molecular dynamics based ion-neutral collisions in an open simulation framework (IDSimF)

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Introduction

In ion mobility spectrometry (IMS), gas phase ions travel through a gas-filled drift tube with a constant electric field, leading to separation by their characteristic ion mobility. In addition, differential mobility spectrometry (DMS) allows to separate ions by their field dependent mobility. This is done by applying an asymmetric waveform with a low and high field phase along the ion flight path.

There are several software packages available (e.g. MOBCAL [1] and IMoS [2]) which can estimate ion mobilities under low field conditions. However, to correctly predict ion mobilities in DMS and high field IMS simulations it becomes necessary to directly vary the electric field.
The Ion Dynamics Simulation Framework (IDSimF) [3] is an open-source software, which allows to simulate ion trajectories in the context of drift-tube IMS and DMS. It was recently extended by a molecular dynamics based (MD) collision model similar to that of MOBCAL to model ion-neutral collisions along the ion flight path in an advanced way.

Methods

Ion trajectory simulations are carried out with IDSimF using the velocity Verlet integrator.
Ion-neutral collisions are thereby modeled by a molecular dynamics based approach using a trajectory method:

- Ion and background gas are modeled as rigid bodies
  - No vibration or rotation over time
- Both particles trajectory are integrated by solving Newton's equations of motion (sub-integration, see **Fig. 1**)
- Force field is given by a combination of 12-6 Lennard-Jones, ion-induced dipole potential and a quadrupole moment for diatomic nitrogen
  - 12-6 LJ: weak attractive potential and strong repulsion for small distances
  - Ion-induced potential: long-range attraction
  - Quadrupole moment: additional attraction term (N_2)

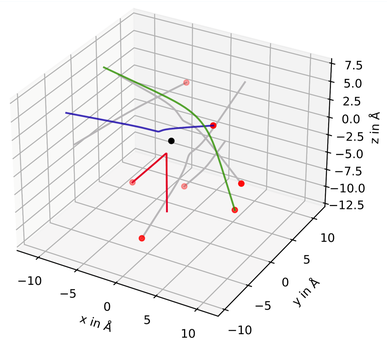

Fig. 1: Exemplary trajectories of background gas particles

IMS Simulations

- Ion mobility K: ratio of ion drift velocity to magnitude of electric field

Drift tube IMS simulations (Fig. 2 and Fig. 3) for varying electric fields (background gas p=20 mbar, T=298 K):

- Significant improvement in ion mobility predictions with MD model compared to simple hard-sphere elastic collisions
- Good agreement with experimental measurements [4-5]

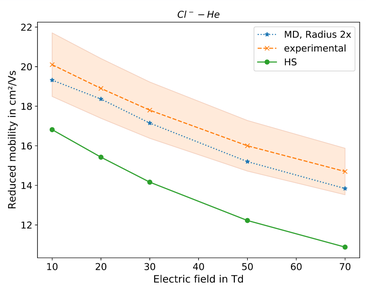

Fig. 2: Comparison of ion mobilities between MD, HS and experiment for Cl^- in He

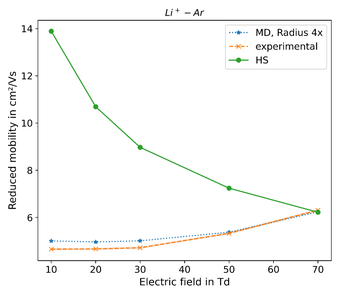

Fig. 3: Comparison of ion mobilities between MD, HS and experiment for Li^+ in Ar

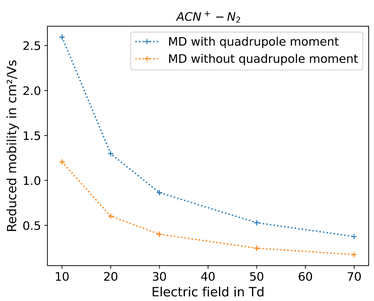

Fig. 4: Comparison of ion mobilities obtained with the MD model with/without quadrupole moment

- First simulations with diatomic nitrogen as background gas were carried out (**Fig. 4**)
  - Protonated acetone was used as the ion (smaller aggregates exhibit numerical instabilities in diatomic nitrogen)
  - Inclusion of the quadrupole moment of N_2 illustrates a notable difference in predicted ion mobilities
  - For this system, the quadrupole moment leads to an overall increase of the ion mobility
  - Experimental measurements with a HiKE-IMS [6] will follow to verify the simulation results

DMS Simulations

DMS simulations to obtain compensation voltages for varying separation voltages at atmospheric pressure:

- **Fig. 5** shows dispersion plots for O_2^+ in Helium for the MD model and the HS model
  - Both models show a hard-sphere trend of the system
  - The MD model shows a weaker hard-sphere trend as the additional attractive forces have an impact on the collision dynamics

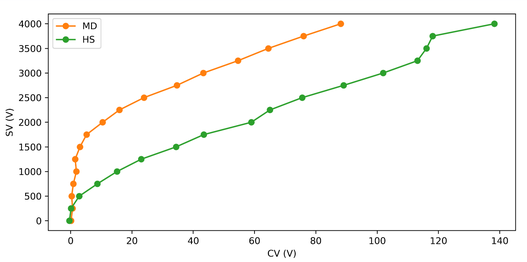

Fig. 5: DMS dispersion plot for the MD model and HS model for O_2^+ in He

- **Fig. 6** shows dispersion plots for the MD model with changes in the polarizability of the background gas (Helium, α = 0.205 Å^3)
  - Decrease of the polarizability by 10% leads to harder collisions and the system shows a stronger hard-sphere trend
  - Increase of the polarizability by 10% leads to softer collisions
  - The increase of the polarizability additionally changes the trend of the system to type B (combination of hard-sphere effects and polarizability effects)

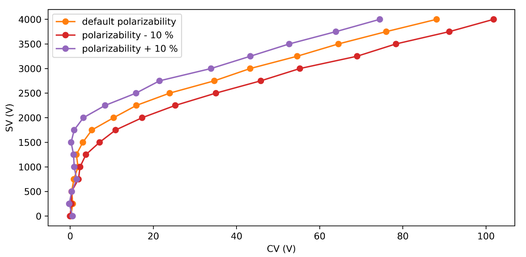

Fig. 6: DMS dispersion plot for the MD model for O_2^+ in He with varied polarizabilities for Helium

Conclusion

- IMS simulations in Helium and Argon show a good agreement with experimental measurements for small ions
- Quadrupole moment has significant impact on ion mobility in systems with N_2
  - In the future HiKE-IMS measurements will be carried out to verify simulations
- DMS simulations can reproduce basic dispersion plot trends
  - Changes in the type of the system are also visible by change of the polarizability

References

[1] A. A. Shvartsburg, M. F. Jarrold: An exact hard-spheres scattering model for the mobilities of polyatomic ions. Chem. Phys. Lett., 1996, 261 , 86 —91.
[2] C. Larriba, C.J. Hogan: Ion mobilities in diatomic gases: measurement versus prediction with non-specular scattering models. J. Phys. Chem. A 117, 3887-3901 (2013).
[3] W. Wißdorf, D. Erdogdu, M. Thinius, T. Benter: Ion Dynamics Simulation Framework (IDSimF). ASMS 2020, Online reboot.
[4] H.W. Ellis, R.Y. Pai, E.W. McDaniel, E.A. Mason, L.A. Viehland: Transport properties of gaseous ions over a wide energy range. Atomic Data and Nuclear Data Tables, Volume 17, Issue 3, 1976, Pages 177-210.
[5] L.A. Viehland, E.A. Mason; Transport properties of gaseous ions over a wide energy range, IV. Atomic Data and Nuclear Data Tables, Volume 60, 1995, Pages 37-95.
[6] J. Langejuergen, M. Allers, J. Oermann, A. Kirk, S. Zimmermann: High Kinetic Energy Ion Mobility Spectrometer: Quantitative Analysis of Gas Mixtures with Ion Mobility Spectrometry. Analytical Chemistry 2014 *86* (14), 7023-7032