

Ab-initio approach to differential mobilities - structures, energies and collision cross sections of clustered tetraalkylammonium ions



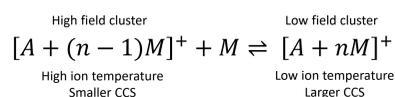
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Introduction

Differential mobility spectrometry (DMS, FAIMS) separates charged compounds based on different gas phase mobilities at "high" and "low" electrical field conditions. Particularly in combination with mass spectrometry this technique sees increasing interest.

In selected applications "chemical modifiers" (M), in essence abundant gas phase concentrations of neutral volatile compounds, are added to alter the mobility of ions (A). We propose that this creates highly dynamic and diverse cluster/decluster processes, changing the collision cross section (CCS), under periodically changing electrical field conditions.



With changing ion temperature (induced by the electric field), the cluster distribution and hence the mobility periodically changes as well, depending on the binding energy and CCS change by a modifier ligand.

A theoretical approach is presented here to model the overall differential mobility of an ion as the sum of the weighted mobilities of possible cluster structures at different ion temperatures.

As a case study, tetra-alkylammonium (R_4N^+) ions were selected as well as different "chemical modifiers", since reliable experimental data are available in the literature.^[1] Initially, only Me_4N^+ was investigated with methanol (MeOH), iso-propyl alcohol (IPA) and acetone (ACE) as modifiers. They all show different dispersion plots (compensation voltage CV, vs. separation voltage SV), which, in our understanding, can be explained by either different changes in CCS by similar binding energy (MeOH - IPA) or different binding energy by similar change in CCS (IPA - ACE).

To simplify the analysis, we assume that the clustering/declustering reactions are fast compared to the change of the electric field (approx. 10^6 Hz). Further, we assume thermal equilibrium with a given ion temperature in each of the two field states. Since ligand association/dissociation reactions are frequently barrier free, the reactions should be collisionally controlled. Assuming 3 Vol% modifier molecules present in the gas phase, there are sufficient collisions to swiftly reach equilibrium ($>10^8$ Hz).

Computational Details

Software package:

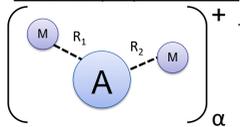
Gaussian09, Revision C.01^[2] for DFT calculations
GaussView 6.0.16^[3] for visualization
MOBCAL^[4] for CCS (N_2 version of Campuzano)
Python scripts for plotting

Machine:

Linux-based computer cluster, 4x16-Core CPUs (6282SE AMD Opteron; Advanced Micro Devices GmbH, Dornach, Germany) and 32x16 GB memory

Methods

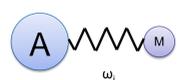
Geometry Optimization:



B3LYP-D/def2-TZVPP with empirical dispersion^[5]

→ structure of cluster α of size n ($[A+nM]^+$)

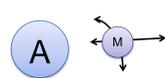
Energies and partition function:



- Harmonic frequency analysis on **B3LYP-D/def2-TZVPP**
- Refined electronic energy on **B2PLYP-D/def2-TZVPP**

→ (total) molecular partition functions Q , Zero-Point Energy E_{ZPE} and electronic energy E_0

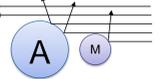
MD Simulation:



- **ADMP method B3LYP-D/def2-SVP**
- 5000 x 0.2 fs steps
- E_{ZPE} used as kinetic energy

→ sampling of accessible configurational space

CCS calculation:



- **40 random config. from MD**
- In N_2 @ $T = 423.15$ K

→ CCS distribution f_{CCS} and average \overline{CCS}

Quantum Harmonic Superposition Approximation:

- For each molecule $[A+nM]^+$ calculate:

- **Energy level $E(n, \alpha)$**

$$E(n, \alpha) = [E_0 + E_{ZPE}]_{[A+nM]^+} + (\tilde{n} - n)[E_0 + E_{ZPE}]_M$$

- **Molecular partition function $Q(n, \alpha)$ calc. at ion temperature $\vartheta = T + m_{N_2} v_D^2 / 3k_B$**

$$Q_\vartheta(n, \alpha) = Q_\vartheta([A + nM]^+) \cdot Q_T(M)^{\tilde{n}-n}$$

- **Q-HSA^[6] partition function $Z(n, \alpha)$**

$$Z_\vartheta(n, \alpha) = \left(\frac{[M]}{N}\right)^n Q_\vartheta(n, \alpha) \cdot \exp\left(-\frac{\Delta E(n, \alpha)}{k_B \vartheta}\right)$$

- **Canonical probability $P(n, \alpha)$**

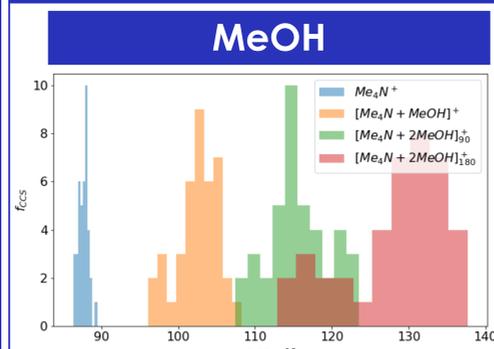
$$P_\vartheta(n, \alpha) = Z_\vartheta(n, \alpha) / \sum_n \sum_\alpha Z_\vartheta(n, \alpha)$$

- **Weighting to a canonical average $\langle K \rangle_{h/l}$**

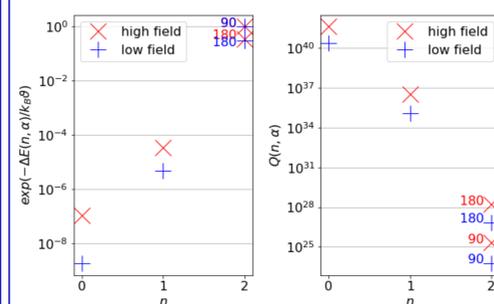
$$K_\vartheta(n, \alpha) = \frac{\sqrt{18\pi}}{16} \cdot \frac{1}{m} + \frac{1}{m_{N_2}} \cdot \frac{ze}{\sqrt{k_B \vartheta \overline{CCS}(n, \alpha)}} \cdot \frac{1}{N}$$

$$\langle K \rangle_{h/l} = \sum_n \sum_\alpha K_{h/l}(n, \alpha) \cdot P_{h/l}(n, \alpha)$$

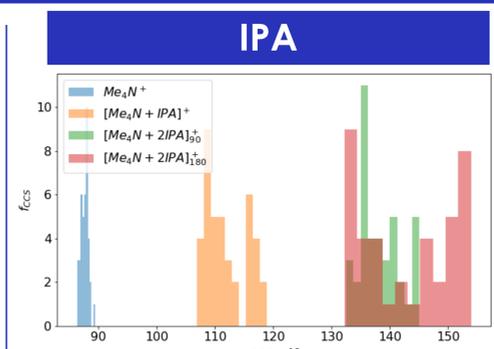
Analysis



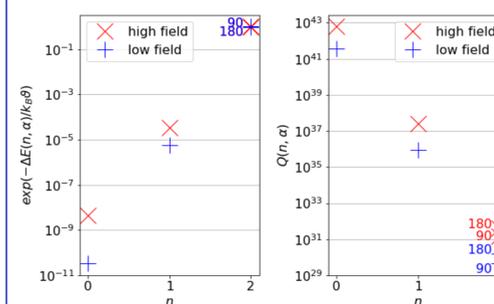
- Increase in CCS is smaller than for IPA, ACE
- Dispersed distributions
- 90° configuration is largely different from 180°



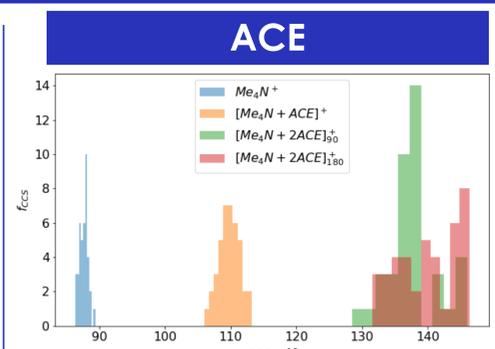
- Binding energy 0.34 eV
- Boltzmann factor is higher for "high field" due to larger temperature
- Partition function reduces with n due to loss of translational states; is also smaller in "low field"
- $\langle n \rangle_l = 0.00$, $\langle n \rangle_h = 0.00$
- Mostly bare ion present



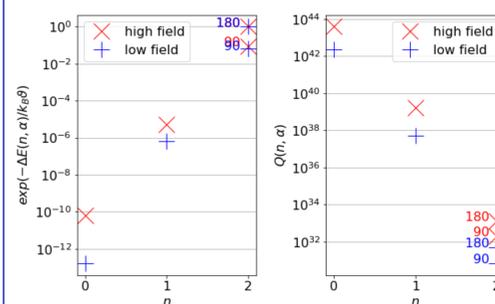
- Larger increase than for MeOH, similar to ACE
- Has the largest overall CCS
- 90° and 180° configuration are comparable



- Binding energy 0.52 eV
- No difference in 90°/180° configurations in energy and partition function
- $\langle n \rangle_l = 0.01$, $\langle n \rangle_h = 0.00$
- Mostly bare ions

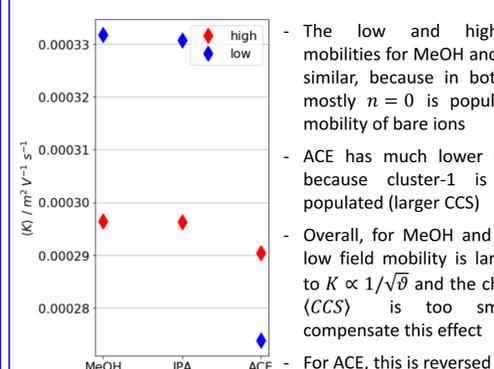


- Larger increase than for MeOH, similar to IPA
- Distributions are rather narrow
- 90° and 180° configuration are comparable



- Binding energy 0.65 eV
- Partition function of 180° configuration is always larger
- $\langle n \rangle_l = 0.76$, $\langle n \rangle_h = 0.10$
- Mostly cluster-1 populated in low field, but bare ion in high field
- No significant difference between high and low field

Comparison of $\langle K \rangle_{h/l}$



- The low and high field mobilities for MeOH and IPA are similar, because in both cases mostly $n = 0$ is populated → mobility of bare ions
- ACE has much lower mobility because cluster-1 is mostly populated (larger CCS)
- Overall, for MeOH and IPA the low field mobility is larger due to $K \propto 1/\sqrt{\vartheta}$ and the change in $\langle CCS \rangle$ is too small to compensate this effect
- For ACE, this is reversed

Discussion

Discussion:

- The experimental data showed $\langle K \rangle_l < \langle K \rangle_h$ for all species at a separation voltage of 2000 V (used here as well), this is only reproduced for ACE
- The higher field strength (resulting in a higher ion temperature: $\vartheta_h \approx 520$ K, $\vartheta_l \approx 450$ K) does not change $\langle n \rangle$ for MeOH and IPA since the binding energy is too low to even form clusters in the low field
- For ACE, however, the clusters are stable enough to populate cluster-1 in the low field. Shifting this distribution under higher field conditions changes the mean mobility to higher values
- Under the given results, cluster-2 is rarely populated. The sum over all Z is thus nearly converged

Possible sources of error:

- Because of the weak binding (lack of a clear binding site) the potential is probably highly anharmonic. Hence, the harmonic-oscillator approximation for the molecular partition function Q used here, is erroneous. Rotovibrational coupling is also possible
- The introduction of $[M]^n$ into the Q-HSA partition function, to account for a concentration dependency of the cluster distribution, is more a good guess than mathematically deduced. Although the population then correctly shifts to higher cluster sizes with increasing $[M]$, the functional dependence may be different
- To the best of our knowledge, the Q-HSA has never been used to model dissociation equilibria. It may be the model is insufficient here

Conclusions

Method:

- MD simulations around equilibrium geometry give a vibrationally averaged CCSs. They should be more accurate than those derived from equilibrium structures
- Geometry and (refined) electronic energies are calculated on a good level of theory. The partition functions, however, are approximated in the usual harmonic-oscillator / rigid-rotor framework which could be insufficient for highly anharmonic clusters
- Q-HSA should be a good method to obtain a distribution of the different cluster species. However, to our knowledge, it has never been used for dissociation equilibria
- The assumption of thermal equilibrium at ion temperatures prevailing at high and low field conditions neglects any kinetic effects. It also neglects the sinusoidal form of the separation voltage in differential mobility spectrometers. An average over one high-low-field cycle with the correct time dependent field should be more accurate

Case study:

- In the experiment, ACE showed the largest difference between high and low field mobilities. This is reproduced in this work. The alcohols bind too weakly to even form clusters at this SV
- It becomes clear that clustering of ions with modifier molecules present strongly influences the differential mobility, if the binding energy is high enough

Outlook

- Improved description of partition functions including anharmonic effects (e.g. ref. [7])
- Investigate the cluster distributions at another set of ion temperatures (lower separation voltage)
- Investigate the $[H+n(H_2O)]^+$ system since there is a larger amount of experimental available
- Testing of our Q-HSA for known cluster distributions

Literature

- [1] Campbell, Zhu, Hopkins (2014): *J. Am. Soc. Mass Spectrom.*, 25(9), 1583–1591
- [2] Frisch et al. (2009): Gaussian09, Revision C.01, Gaussian, Inc., Wallingford CT
- [3] Dennington II, Keith, Millam (2016): GaussView 6.0.16, Semichem, Inc.
- [4] (a) Mesleh et al. (1996): *J. Phys. Chem.*, 100(40), 16082–16086 (b) Shvartsburg, Jarrold (1996): *Chem. Phys. Letters*, 261(1–2), 86–91 (c) Campuzano et al. (2012): *Anal. Chem.*, 84(2), 1026–1033
- [5] Grimme (2006): *J. Comp. Chem.*, 27(15), 1787–1799.
- [6] Calvo et al. (2002): *Chem. Phys. Lett.*, 366(1–2), 176–183.
- [7] Haack et al., Poster No. 14, Proceedings of the 30th ASMS Sanibel Conference on Mass Spectrometry, St. Petersburg, FL, January 25 - 28, 2018.

Acknowledgement

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