First-Principles Modeling of Differential Ion Mobility
# Aiming for Quantitative Prediction

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Theory

Differential Ion Mobility of a fixed conformer driven by the combination of three effects [1]:

Effect	Influence on mobility
Kinetic gas theory	Overall decrease with E/N
Decrease of CCS with T_{eff}	Increase with E/N
Dynamic clustering/declustering	Increase with E/N

High-field: smaller clusters

Low-field: larger clusters
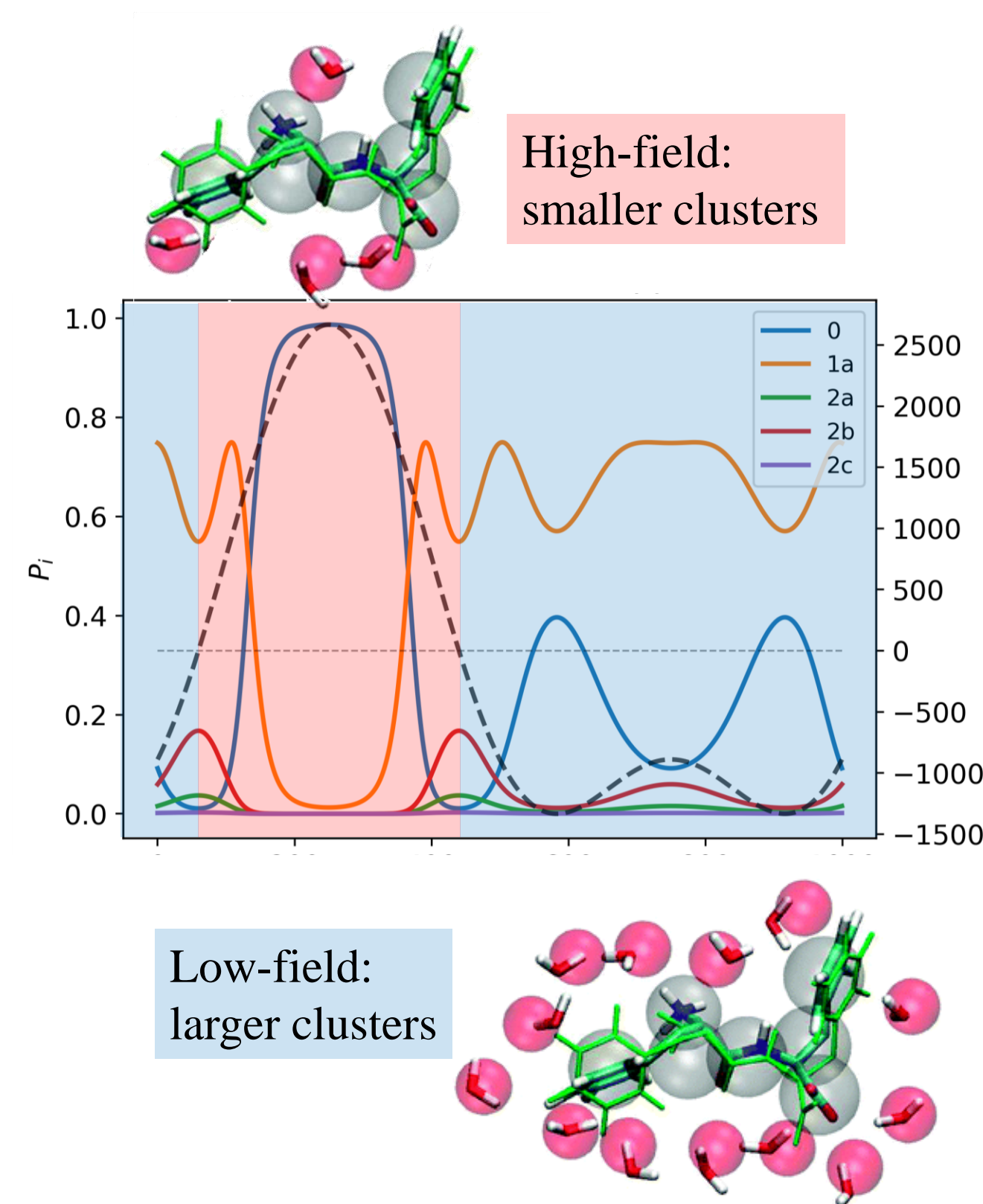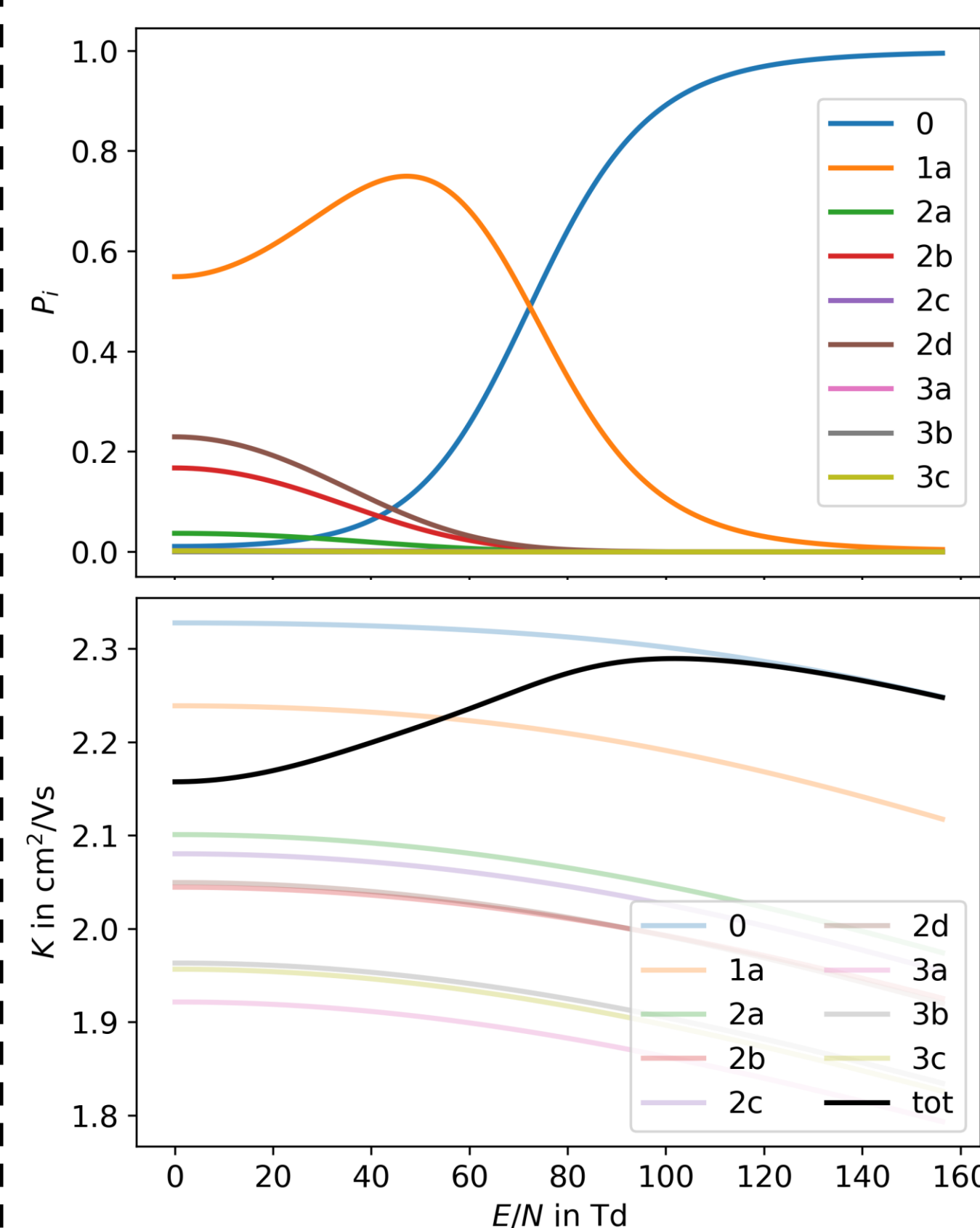
2-Temperature-Theory

$$[K]_1 = \frac{3e}{16N}\left(\frac{2\pi}{\mu k_B T_{eff}}\right)^{1/2}\frac{1}{\Omega^{(1,1)}(T_{eff})}$$

$$[T_{eff}]_1 = T + \frac{M}{3k_B}v_D^2$$

Modeling the ion mobility with **Mason-Schamp equation** but with T_{eff} instead of T. [2] However, this is just a first order approximation and can show **errors up to 10%**.

Higher order approx. have been developed by Viehland & Mason [3] with a **truncation-iteration scheme**. For this, higher order **collision integrals** are needed!
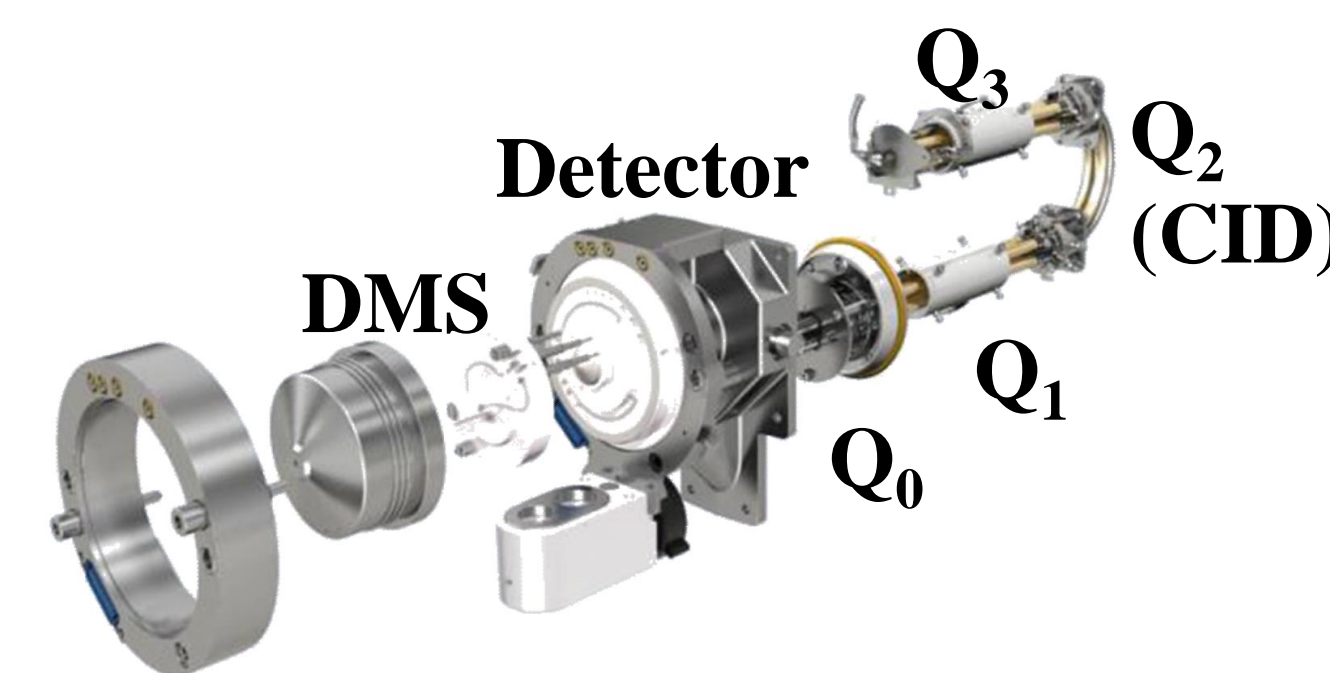
$$Q^{(l)}(g) \propto \int_0^\infty [1-\cos^l(\chi)]b\,\mathrm{d}b$$

$$\Omega^{(l,s)}(T_{eff}) \propto \int_0^\infty g^{2s+3}\exp\left(-\frac{g^2}{k_B T_{eff}}\right)Q^{(l)}(g)\,\mathrm{d}g$$

Experimental

In order to test modeling, experimental dispersion plots were recorded. A set of 23 small drug-like molecules was used to collect experimental and computational data.
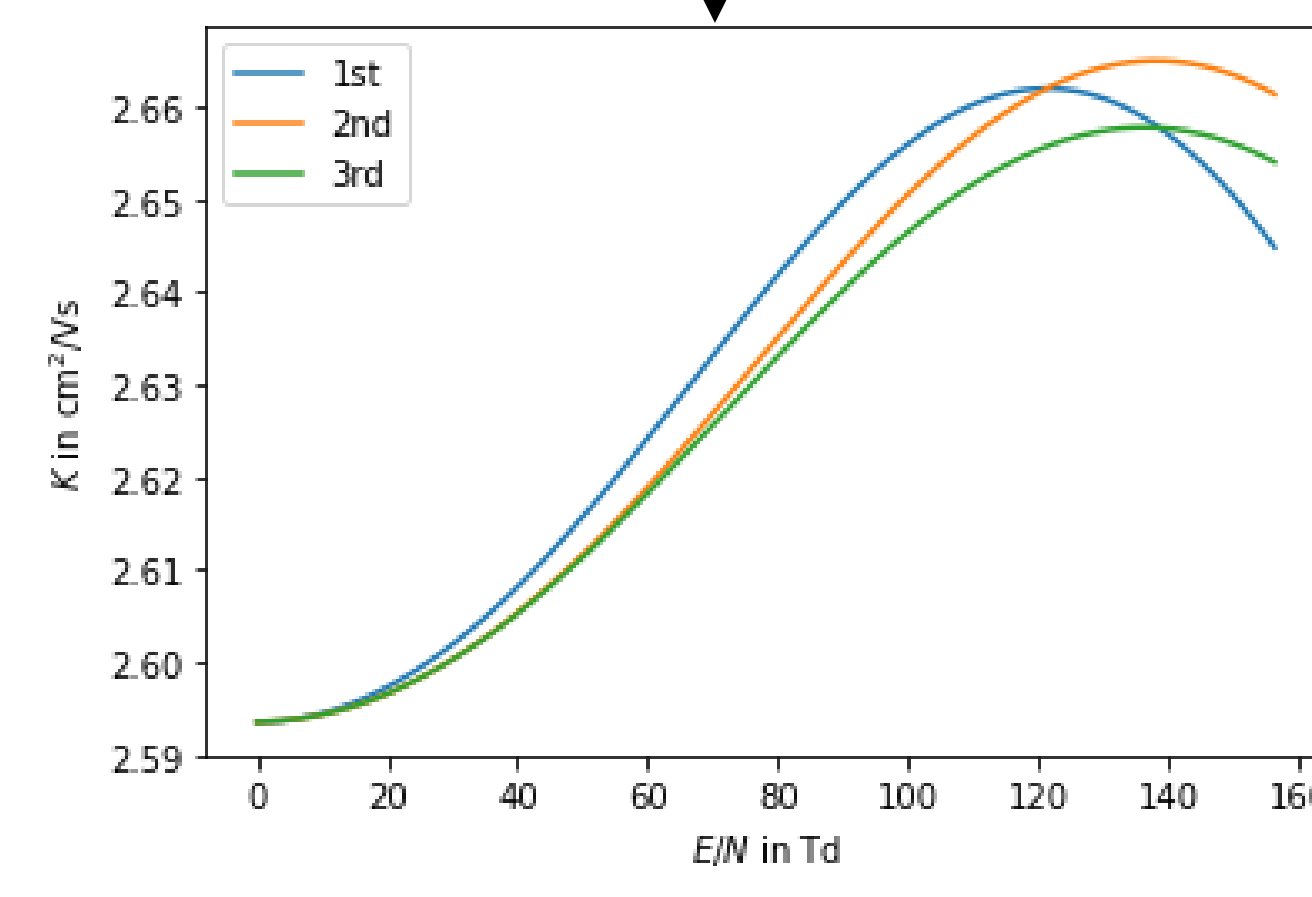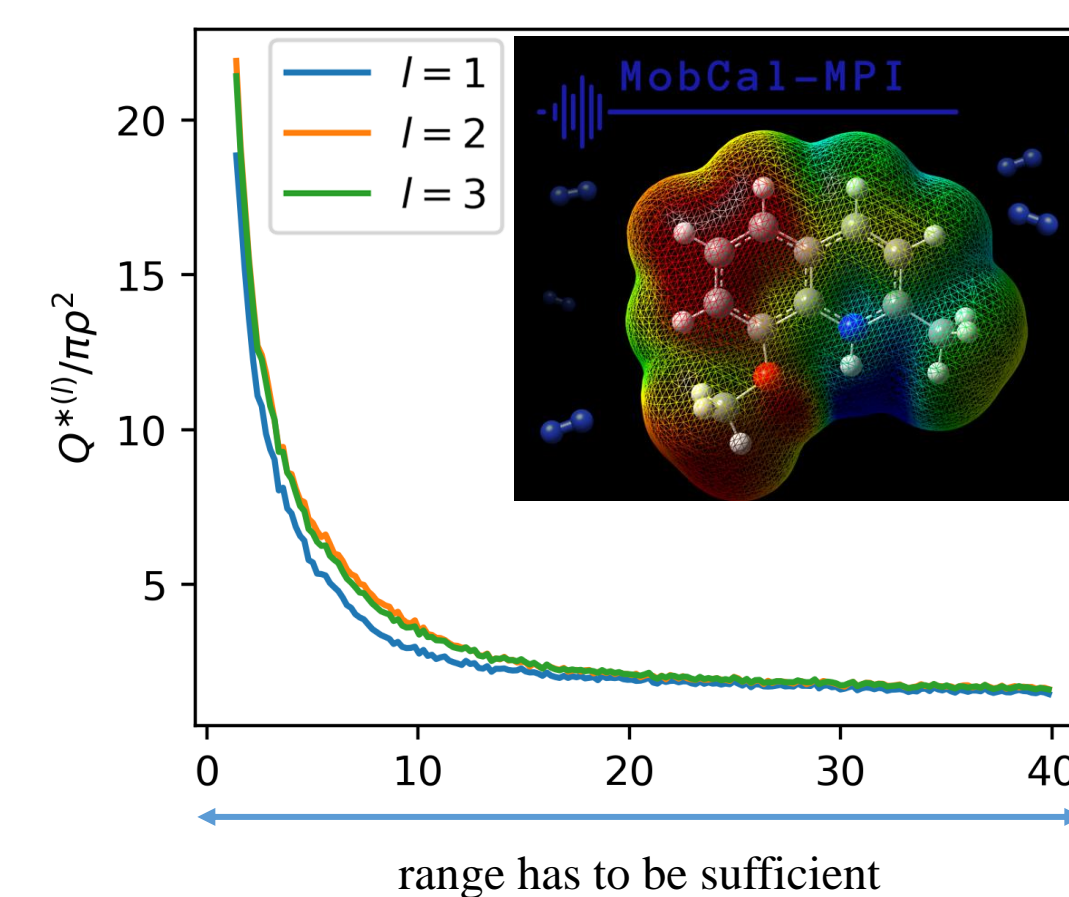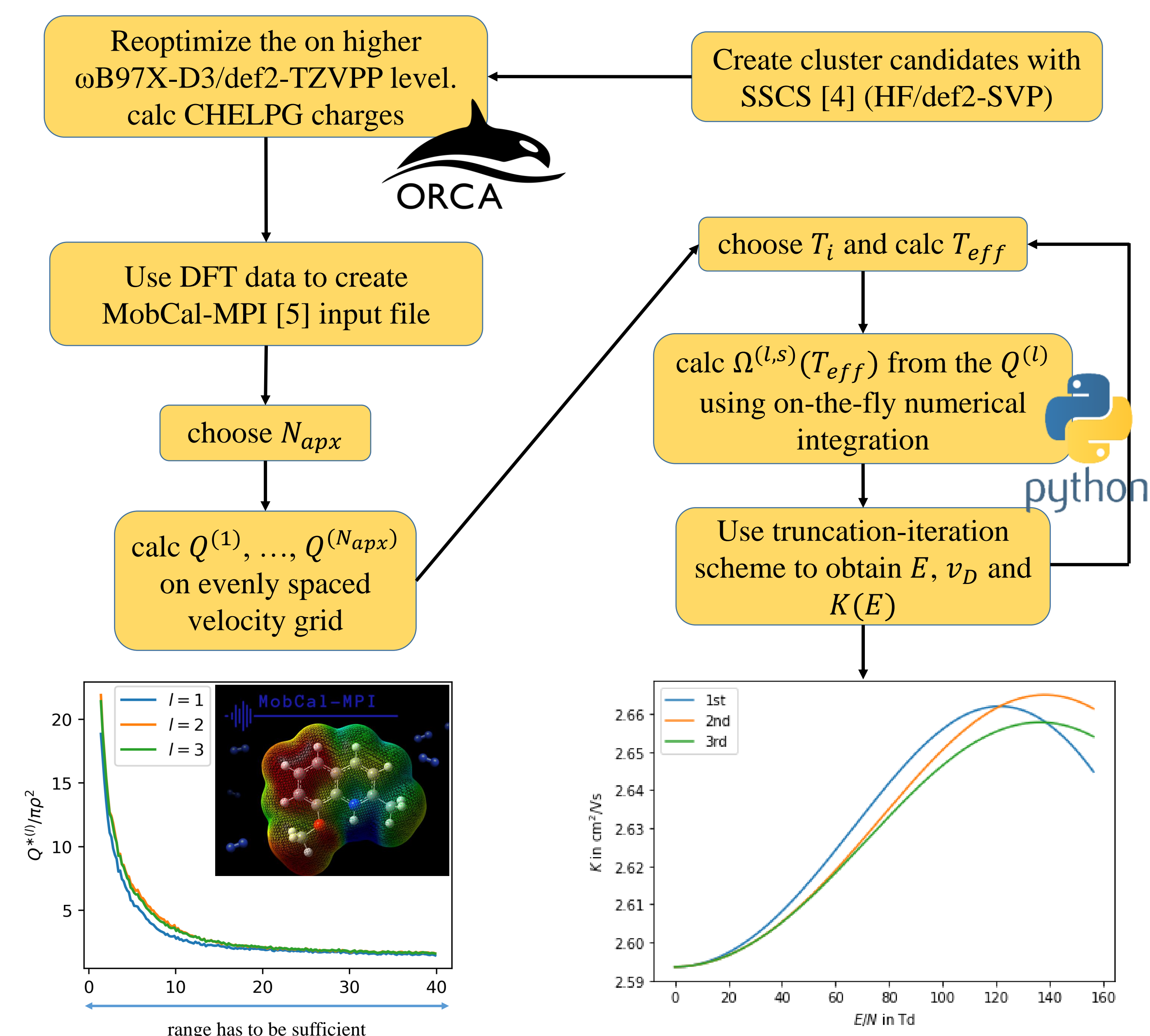
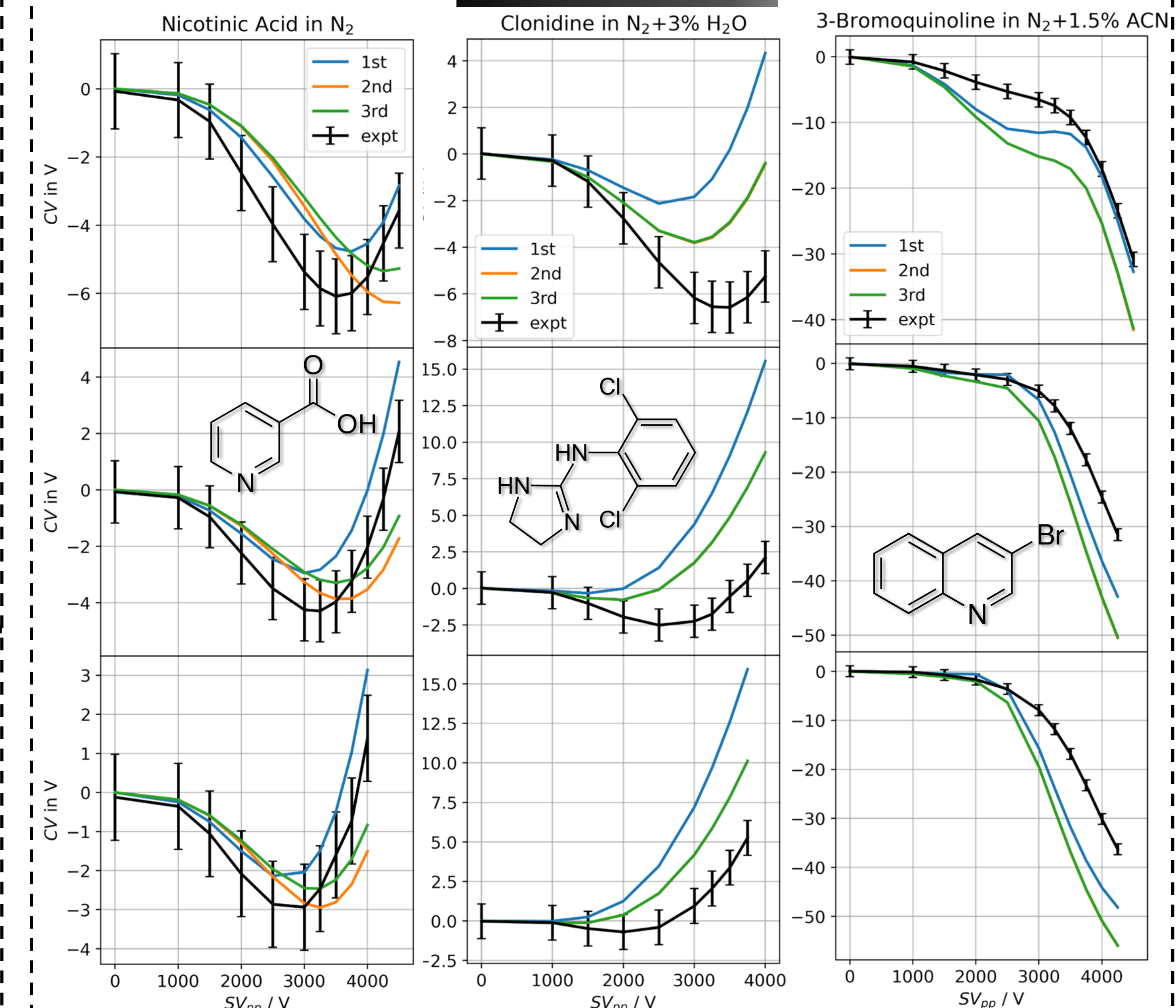The DMS cell was held at one of three temperature settings of Low (150 °C), Medium (225 °C), or High (300 °C).

A SCIEX 5500 QTRAP differential mobility spectrometer instrument was used to obtain all experimental data.

Separation voltages (SVs) ranged from 0 to 4500 V, using step sizes of 250-500 V. At each SV value, the Compensation Voltage (CV) was scanned to create the ionograms. In addition to measurements in pure N_2, scans using H_2O, MeOH, and ACN as chemical modifiers (at concentrations of 1.5, 2.25, and 3.0 mol %) were done.

Computational

Reoptimize the on higher ωB97X-D3/def2-TZVPP level. calc CHELPG charges

Create cluster candidates with SSCS [4] (HF/def2-SVP)

Use DFT data to create MobCal-MPI [5] input file

choose N_{apx}

calc $Q^{(1)}, ..., Q^{(N_{apx})}$ on evenly spaced velocity grid

choose T_i and calc T_{eff}

calc $\Omega^{(l,s)}(T_{eff})$ from the $Q^{(l)}$ using on-the-fly numerical integration

Use truncation-iteration scheme to obtain E, v_D and $K(E)$

range has to be sufficient
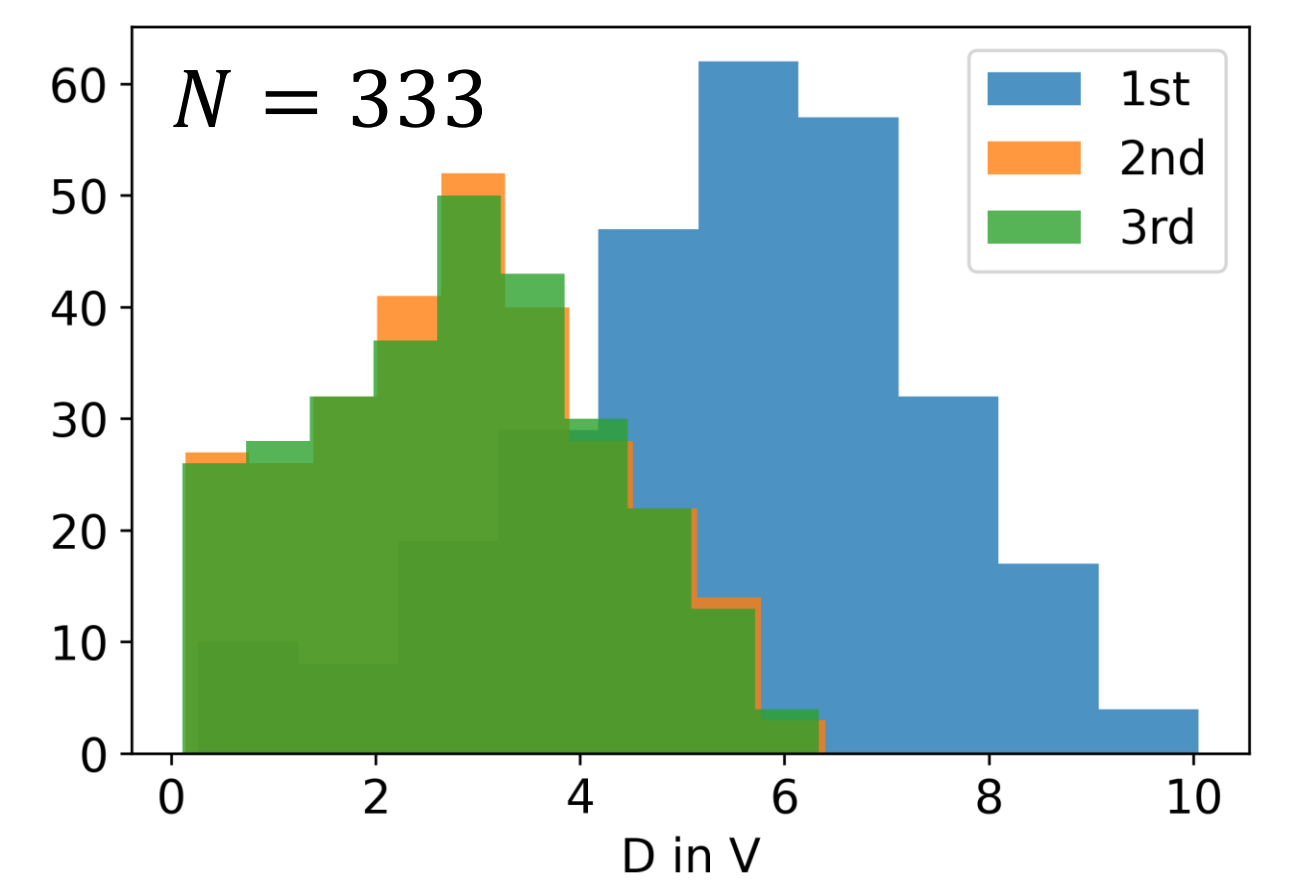
Results/Conclusions

Comparison of experimental and calculated dispersion plots for different systems (with and without chemical modifiers). Top row is at $T = 373$K, middle row is at $T = 423$K, bottom row is at $T = 450$K.
The data is always qualitatively reproduced, sometimes quantitatively. Accurate thermochemistry is needed, otherwise large errors can occur. Non-traditional fine-structure is reproduced (top-right). Changes with temperature are reproduced.

Using the test-set data and another database [6], the overall performance of the higher order approximations was tested. Only non-clustering environments were chosen.
- Higher orders reduce RMS by factor of 2
- 2nd and 3rd order approx. perform almost equally

$$D = \sqrt{\frac{\sum(CV_{expt}-CV_{calc})^2}{N_{data}}}$$

$N = 333$

Outlook

- Increase accuracy of thermochemistry by including anharmonic effects
- Try to account for inelastic collisions by modifying the trajectory calculations in MobCal-MPI
- Study kinetic effects of clustering/declustering

References

1. (a) J. Am. Soc. Mass Spectrom. **2019**, 30(12), 2711; (b) J. Am. Soc. Mass Spectrom. **2020**, 31(4), 796.
2. Mason, E.A.; McDaniel, E.W. Transport Properties of Ions in Gases; Wiley-VCH: New York, NY, USA, **1988**.
3. (a) Ann. Phys. (N. Y.) **1975**, 91(2), 499; (b) Ann. Phys. (N. Y.) **1978**, 110(2), 287.
4. SSCS (Systematic Sampling of Cluster Surfaces), unpublished work
5. (a) J. Phys. Chem. **1996**, 100(40), 16082; (b) Chem. Phys. Lett. **1996**, 261(1–2), 86; (c) Analyst **2019**, 144(5), 1660.
6. Analyst **2021**, 146(15), 4737.