

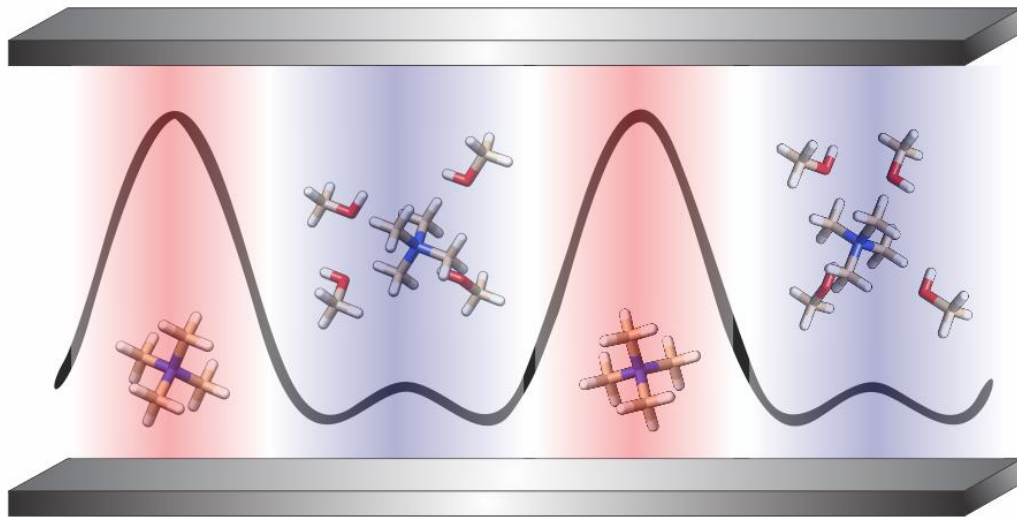
A First Principles Model of Differential Ion Mobility: The Effect of Ion-Solvent Clustering

SCP 2019, University of Waterloo

Alexander Haack^a, Jeff Crouse^b, Femke-Jutta Schlüter^a,
Thorsten Benter^a, W. Scott Hopkins^b

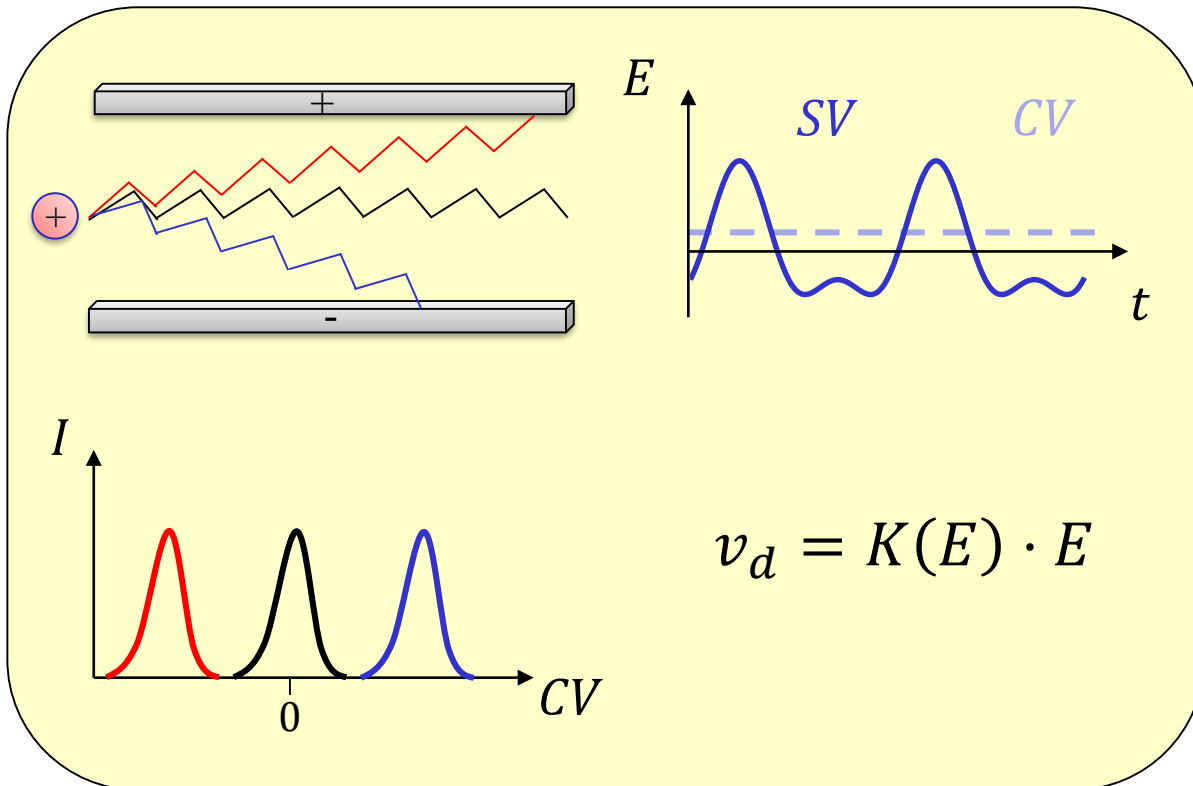
^a University of Wuppertal, Germany

^b University of Waterloo, ON, Canada

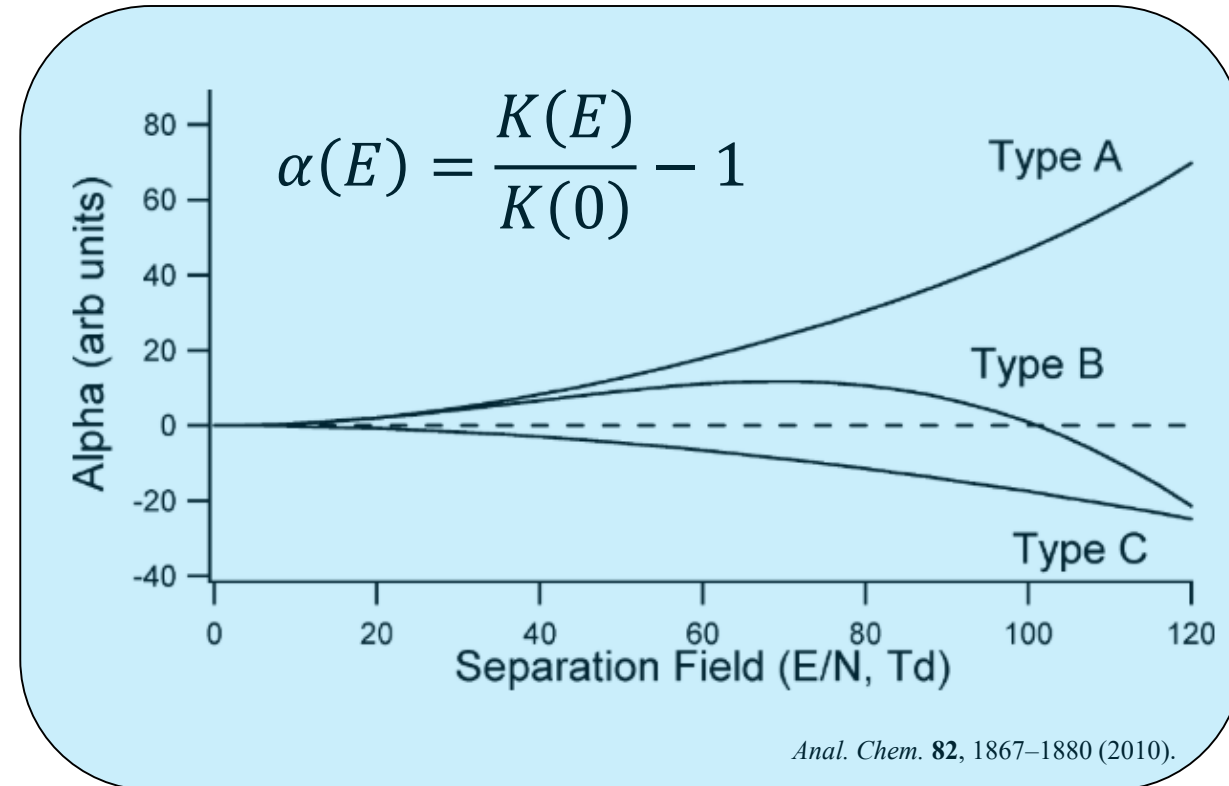


DIFFERENTIAL MOBILITY SPECTROMETRY (DMS)

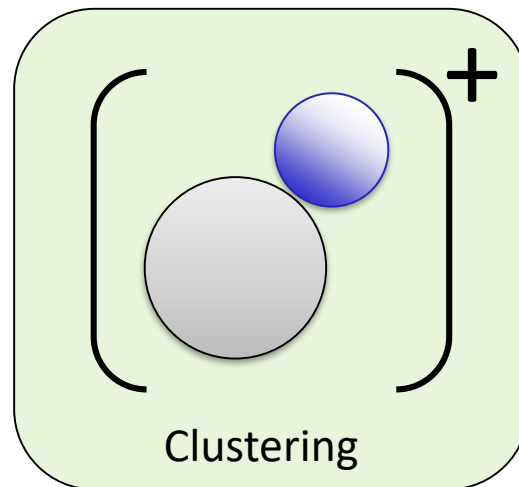
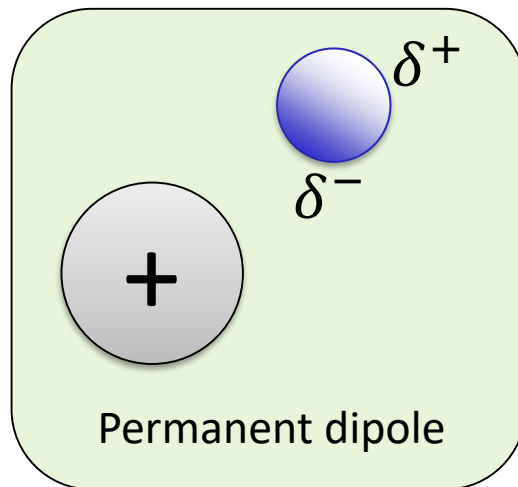
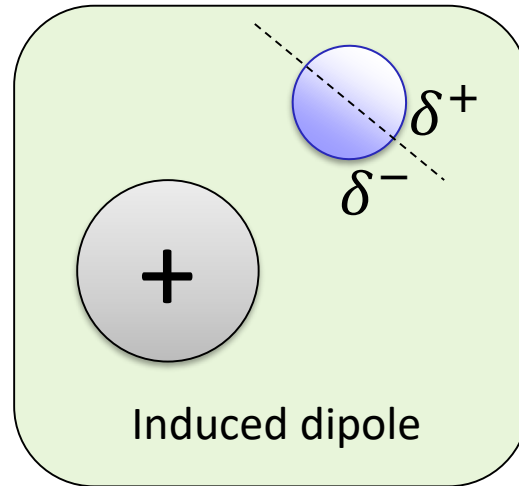
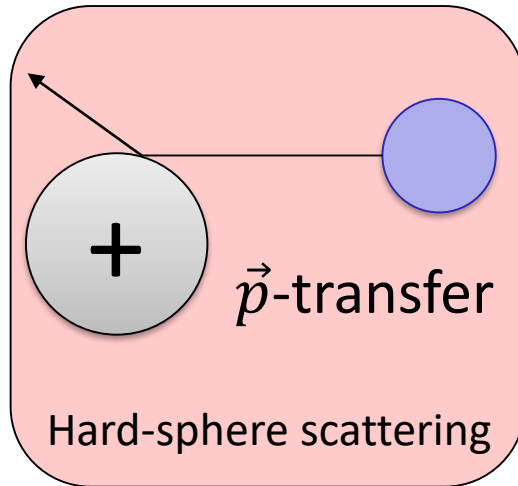
- DMS as pre-filter for mass spectrometry



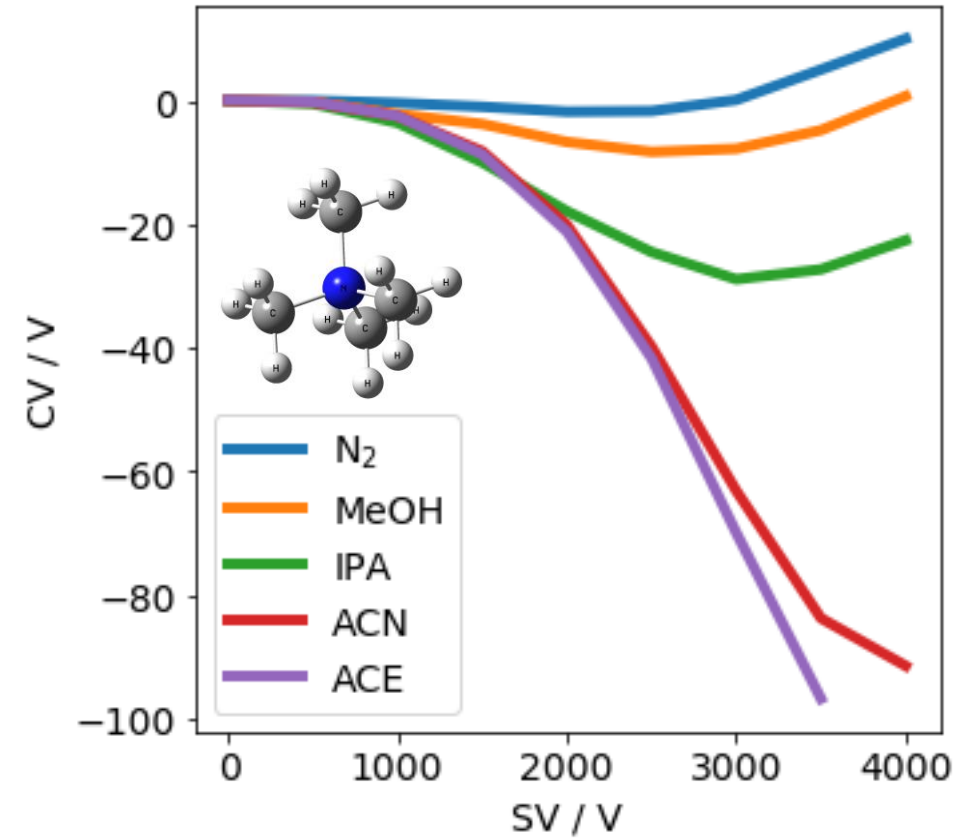
- Understand the field dependency of $K(E)$



DIFFERENTIAL MOBILITY SPECTROMETRY



In N₂ with 1.5% v/v solvents



J. Am. Soc. Mass Spectrom. **25**, 1583-1591 (2014).

MODELING OF MOBILITY: COLLISION CROSS SECTION

- Mason-Schamp eq.

$$K = \frac{3}{16} \left(\frac{2\pi}{\mu k_B T} \right)^{1/2} \frac{ze}{N\Omega(T)}$$

MobCalc-MPI (from Hopkins lab)

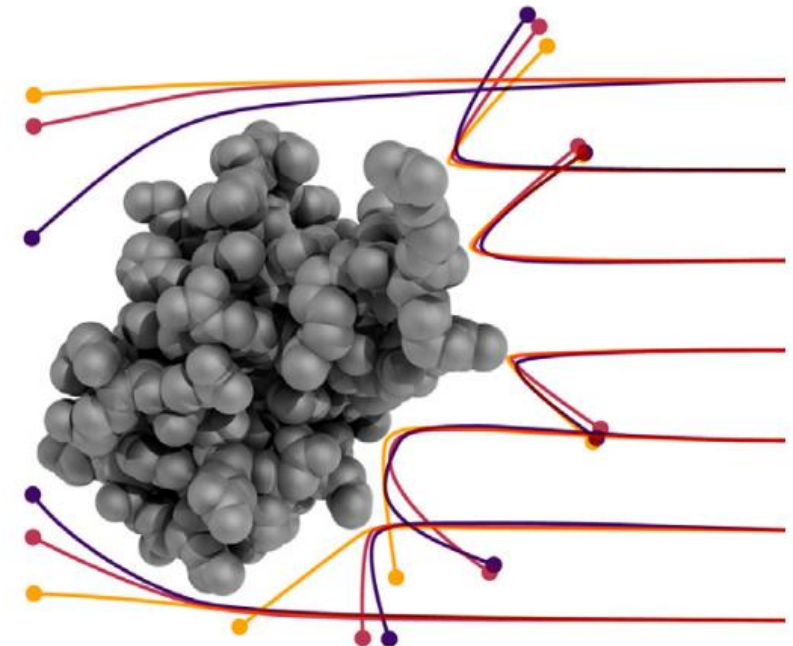
$$\Omega(T) = \frac{1}{8\pi^2} \int_0^{2\pi} d\theta \int_0^\pi \sin\varphi d\varphi \int_0^{2\pi} d\gamma \frac{\pi}{8} \left(\frac{\mu}{k_B T} \right)^3$$

$$\times \int_0^\infty \exp\left(-\frac{\mu v_r^2}{2k_B T}\right) v_r^5 dv_r \int_0^\infty 2b(1 - \cos(\chi(\theta, \varphi, \gamma, v_r, b))) db$$

Analyst **144**, 1660–1670 (2019).

J. Phys. Chem. **100**, 16082–16086 (1996).

Chem. Phys. Letters **261**, 86–91 (1996).



Curr. Opin. Chem. Biol. **42**, 51–59 (2018)

MODELING OF MOBILITY: HARD-SPHERE SCATTERING

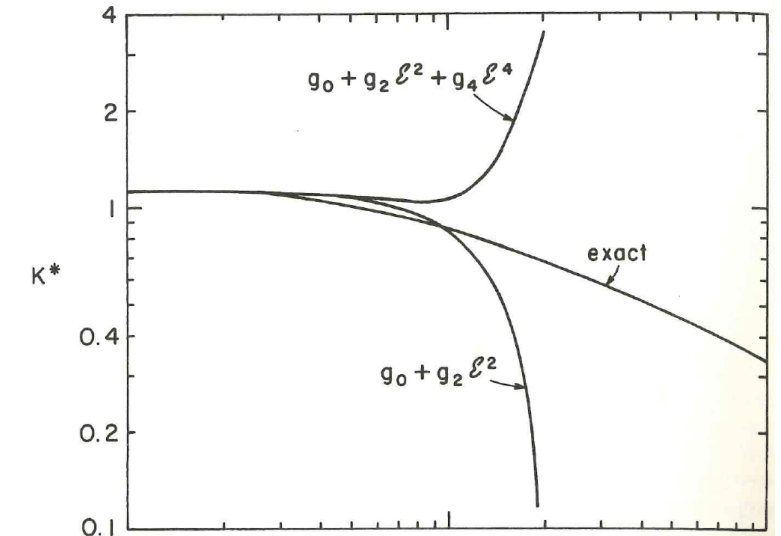
- Mason-Schamp eq. only valid in zero-field limit

$$K_{1T} = \frac{3}{16} \left(\frac{2\pi}{\mu k_B T} \right)^{1/2} \frac{ze}{N\Omega(T)}$$

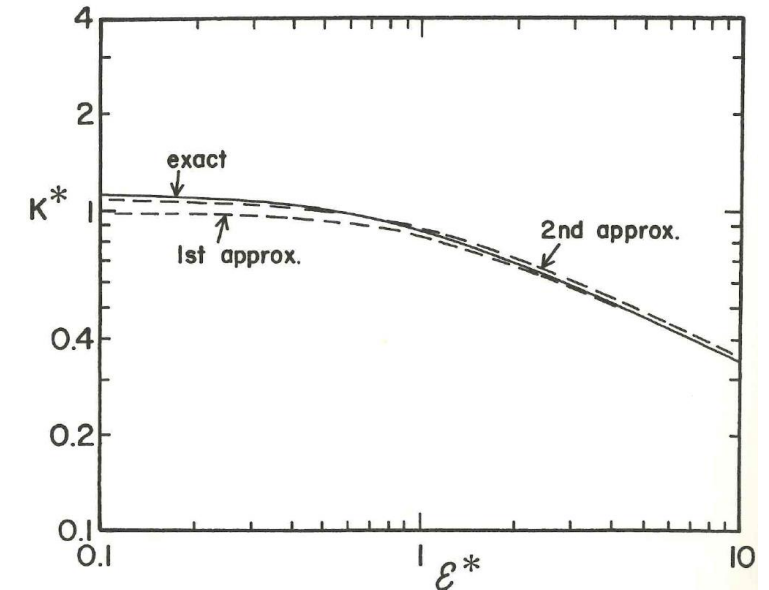
- One improvement: two-temperature theory $T \rightarrow T_{eff}$
– Ions have different velocity distribution

$$K_{2T} = \frac{3}{16} \left(\frac{2\pi}{\mu k_B T_{eff}} \right)^{1/2} \frac{ze}{N\Omega(T_{eff})} \quad T_{eff} = T + \frac{m_b v_d^2}{3k_B}$$

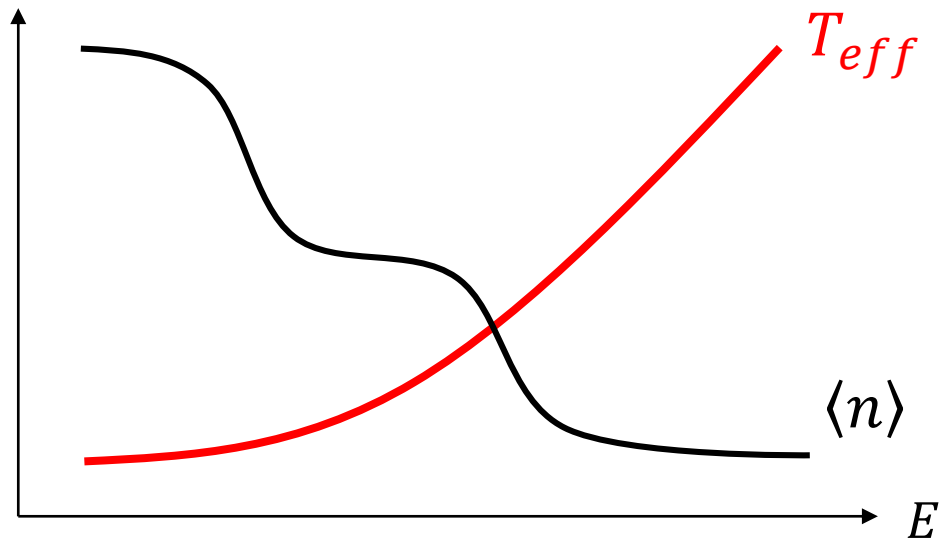
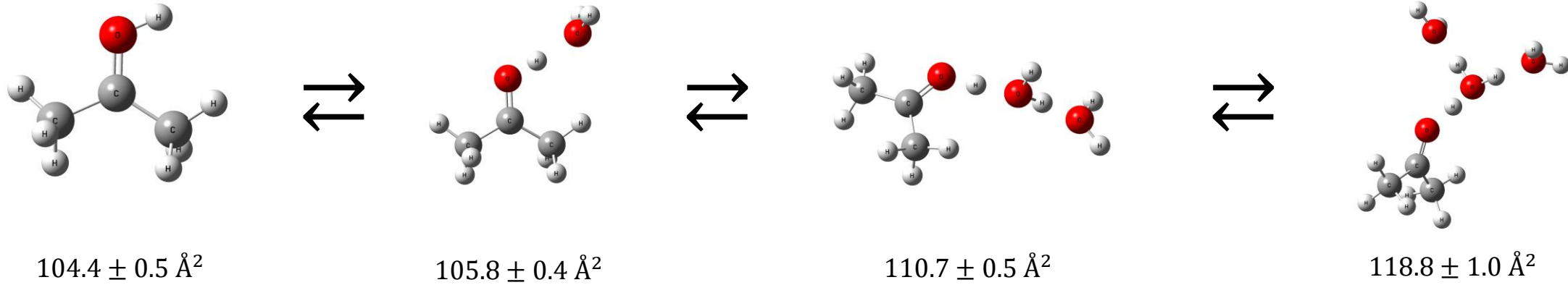
1T-Theory



2T-Theory



MODELING OF MOBILITY: CLUSTERING

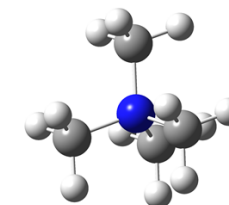
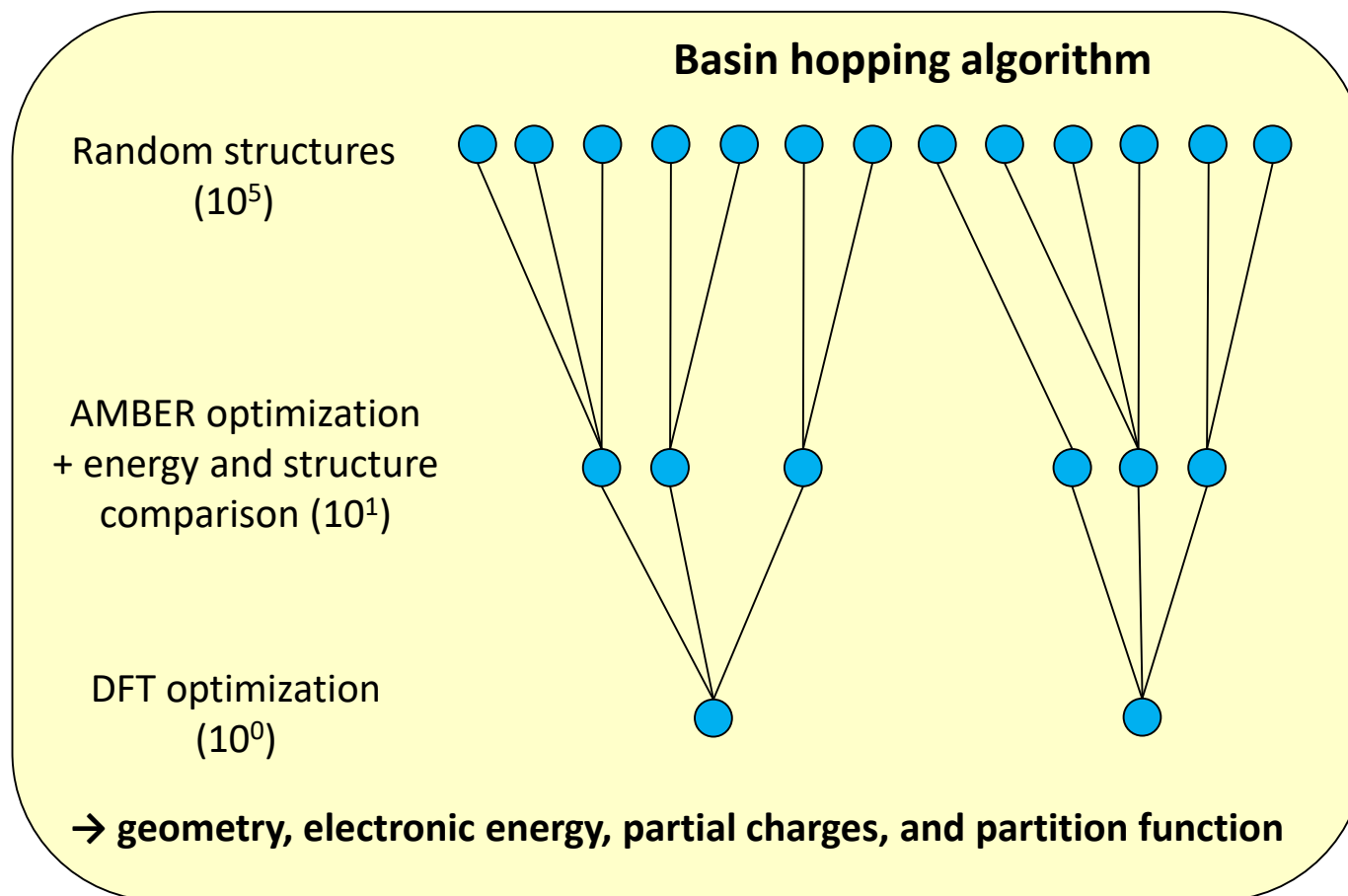


Dynamic equilibrium depending on T_{eff}

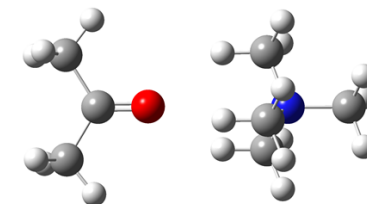
$$K(E) = \sum_i P_i(E) \cdot K_i$$

1.) DETERMINE CLUSTER STRUCTURES

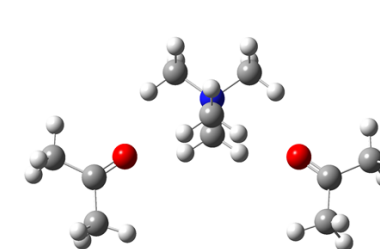
- We need the geometry and partial charges for the MobCalc-MPI input



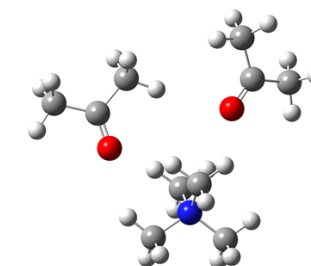
$[\text{Me}_4\text{N}]^+$
0.000



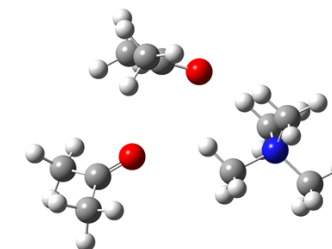
$[\text{Me}_4\text{N}+\text{ACE}]^+$
-0.643



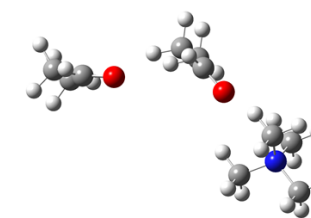
$[\text{Me}_4\text{N}+(\text{ACE})_2]_a^+$
-1.195



$[\text{Me}_4\text{N}+(\text{ACE})_2]_b^+$
-1.092



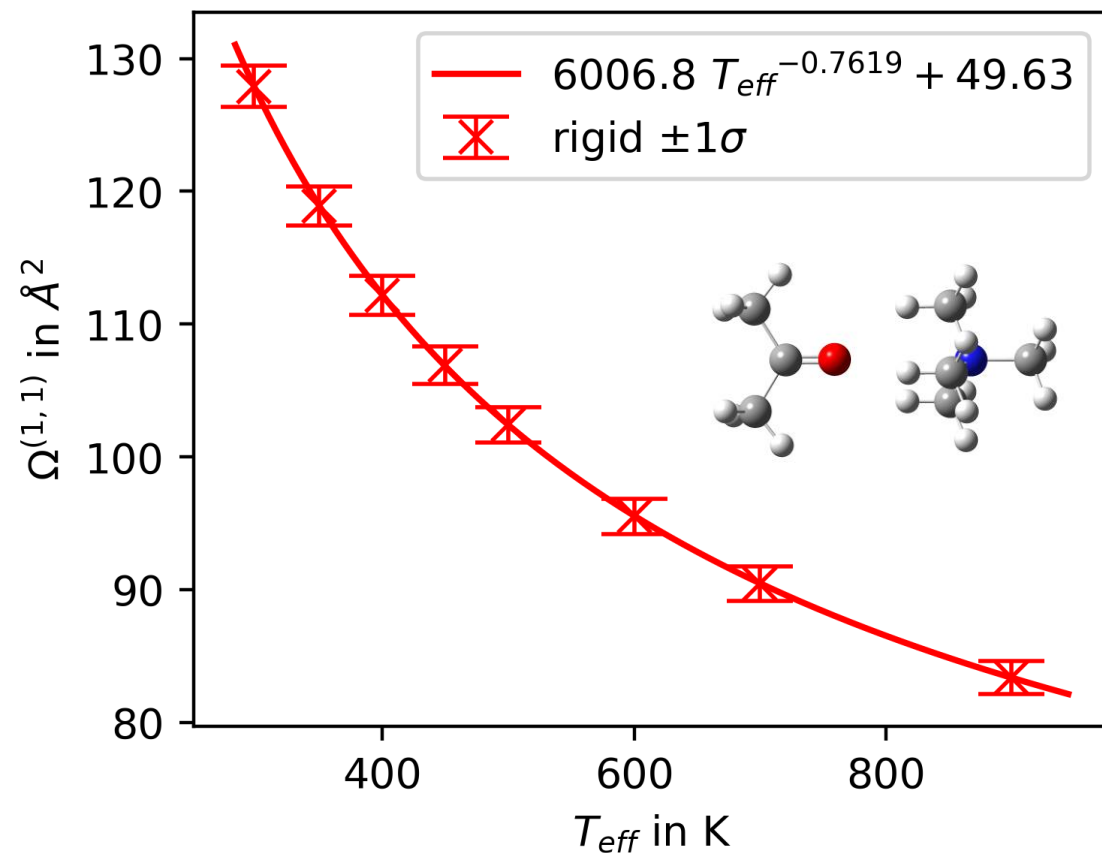
$[\text{Me}_4\text{N}+(\text{ACE})_2]_c^+$
-1.035



$[\text{Me}_4\text{N}+(\text{ACE})_2]_d^+$
-0.969

2.) CALCULATE Ω FOR DIFFERENT T_{eff}

- Fit the data to $\Omega(T_{eff}) = a \cdot T_{eff}^b + c$



Cluster	T range in [K]	a in [$\text{\AA}^2/\text{K}^{-b}$]	b	c in [\AA^2]
Me_4N^+	298 – 1300	6250.7	-0.7587	23.15
$[\text{Me}_4\text{N}+\text{ACE}]^+$	298 – 900	6006.8	-0.7619	49.63
$[\text{Me}_4\text{N}+(\text{ACE})_2]^+_a$	298 – 700	4284.0	-0.6903	68.90
$[\text{Me}_4\text{N}+(\text{ACE})_2]^+_b$	298 – 700	4751.3	-0.7152	66.92
$[\text{Me}_4\text{N}+(\text{ACE})_2]^+_c$	298 – 700	4697.6	-0.7073	65.64
$[\text{Me}_4\text{N}+(\text{ACE})_2]^+_d$	298 – 700	4543.0	-0.6911	69.46
$[\text{Me}_4\text{N}+\text{ACN}]^+$	298 – 900	5956.0	-0.7719	44.63
$[\text{Me}_4\text{N}+(\text{ACN})_2]^+_a$	298 – 700	4556.2	-0.7227	61.95
$[\text{Me}_4\text{N}+(\text{ACN})_2]^+_b$	298 – 700	4928.9	-0.7139	61.88
$[\text{Me}_4\text{N}+(\text{ACN})_2]^+_c$	298 – 700	4380.7	-0.6952	56.05
$[\text{Me}_4\text{N}+(\text{ACN})_3]^+_a$	298 – 700	3725.6	-0.6739	77.73
$[\text{Me}_4\text{N}+\text{MeOH}]^+$	298 – 900	5601.3	-0.7481	36.56
$[\text{Me}_4\text{N}+(\text{MeOH})_2]^+_a$	298 – 700	4076.4	-0.6894	44.77
$[\text{Me}_4\text{N}+(\text{MeOH})_2]^+_b$	298 – 700	5367.5	-0.7467	50.25
$[\text{Me}_4\text{N}+(\text{MeOH})_2]^+_c$	298 – 700	5690.0	-0.7479	50.61

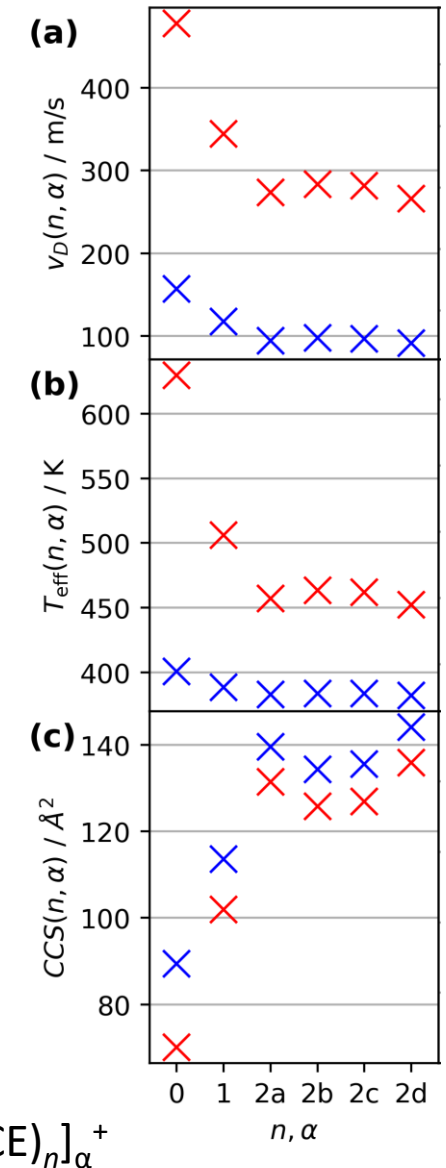
3.) CALCULATE ACTUAL T_{eff} FOR PARTICULAR E

- Use Mason-Schamp and two-temperature theory *self-consistently*

$$v_d = \frac{3}{16} \left(\frac{2\pi}{\mu k_B T_{eff}} \right)^{1/2} \frac{ze}{\Omega(T_{eff})} \cdot \frac{E}{N}$$

$$T + \frac{m_b v_d^2}{3k_B} = T_{eff}$$

For examination, see Poster **5(a)**:
How hot are your ions in Differential Mobility Spectrometry?



— 25 Td
 — 76 Td
 $[\text{Me}_4\text{N}+(\text{ACE})_n]_\alpha^+$

4.) CALCULATE CLUSTER POPULATION

- Modified version of *superposition approximation*

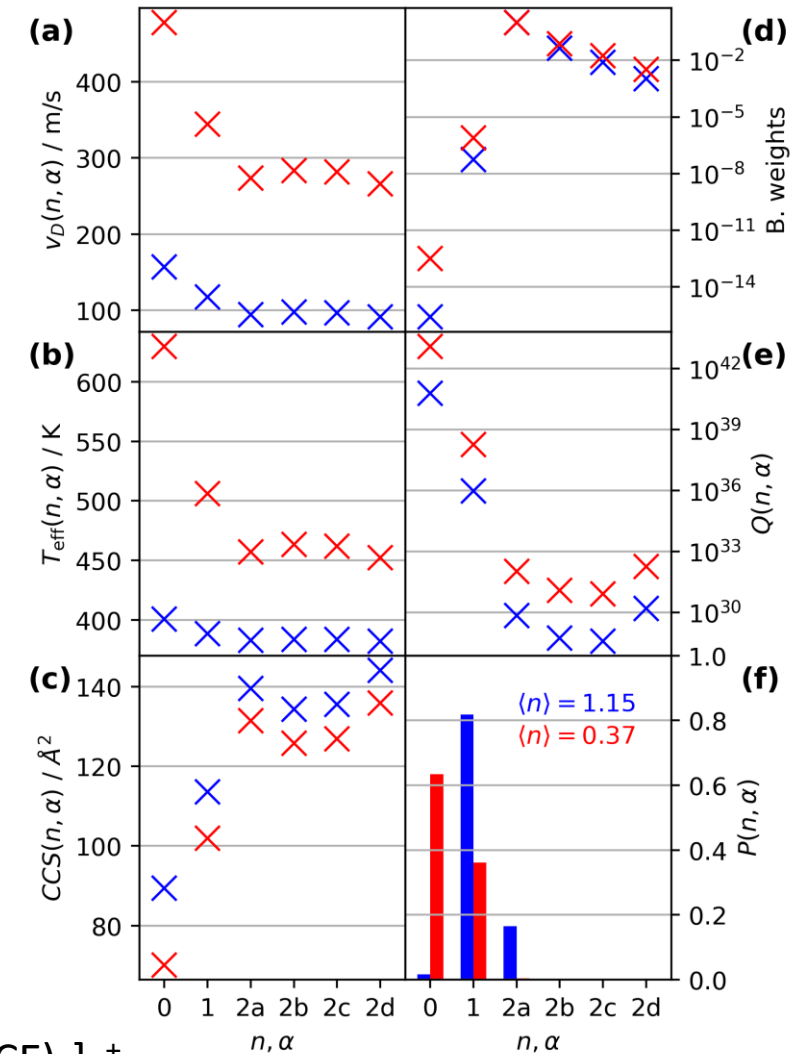
$$Z_1 = \left(\frac{[M]}{N}\right)^{n_1} Q_1(T_1) Q_M(T)^{\tilde{n}-n_1}$$

$$P_i = \frac{Z_i}{\sum_i Z_i}$$

$$Z_i = \left(\frac{[M]}{N}\right)^{n_i} Q_i(T_i) Q_M(T)^{\tilde{n}-n_i} \cdot \exp\left(-\sum_{j=2}^i \frac{\varepsilon_{0,j} - \varepsilon_{0,j-1}}{k_B T_{j-1}}\right) \text{ for } i \geq 2$$

- Right: Mobility *increases* with field strength (Type A)!

— 25 Td
 — 76 Td
 $[\text{Me}_4\text{N}+(\text{ACE})_n]_{\alpha}^{+}$

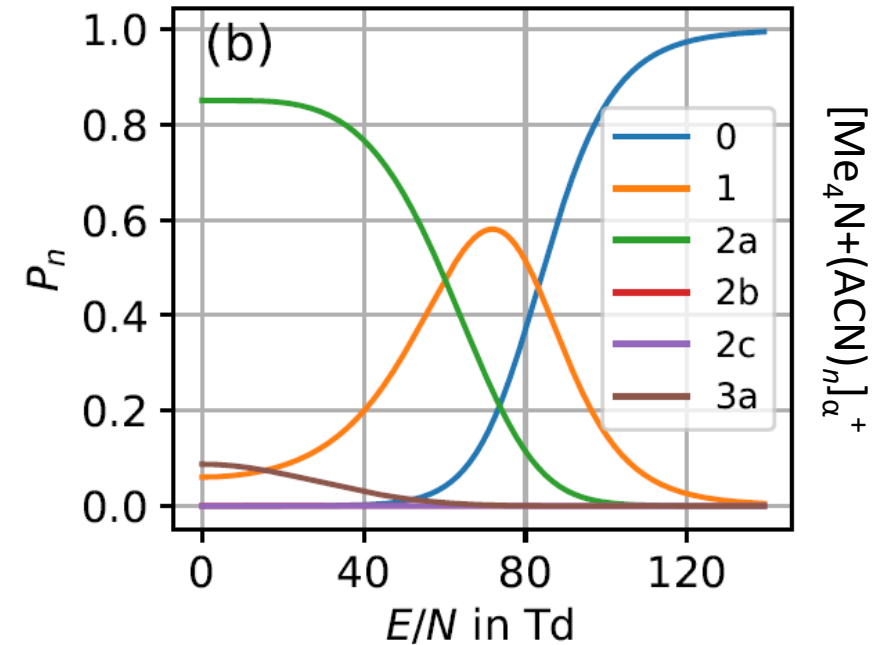
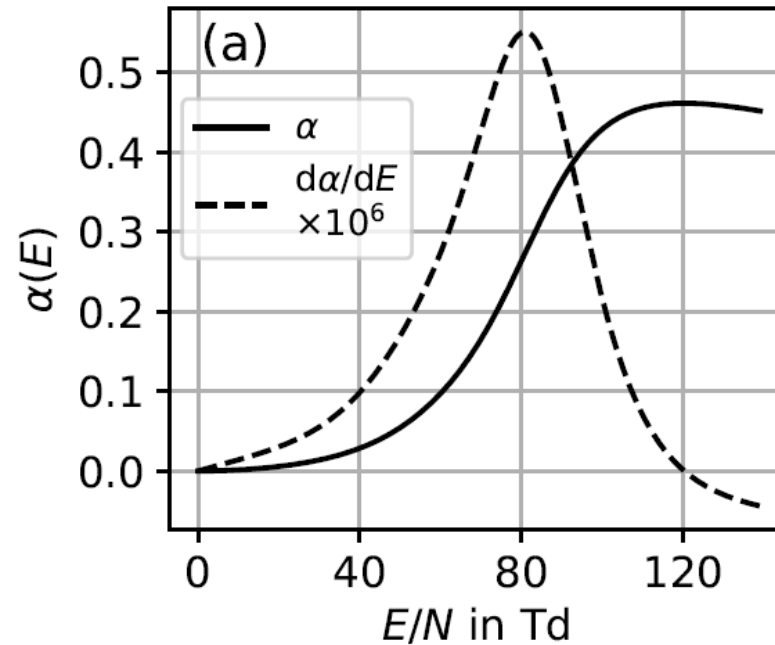


5.) VARY THE FIELD STRENGTH → ALPHA-FUNCTIONS

- For each E , calculate cluster distribution and ensemble mobility

$$K(E) = \sum_i P_i(E) \cdot K_i$$

$$\alpha(E) = \frac{K(E)}{K(0)} - 1$$



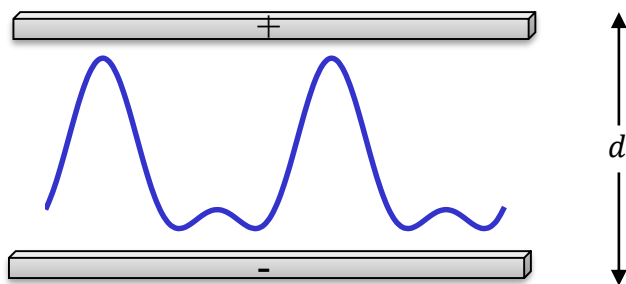
- Cluster size decreases → mobility increases (Type A)!

6.) DETERMINE DISPERSION PLOTS

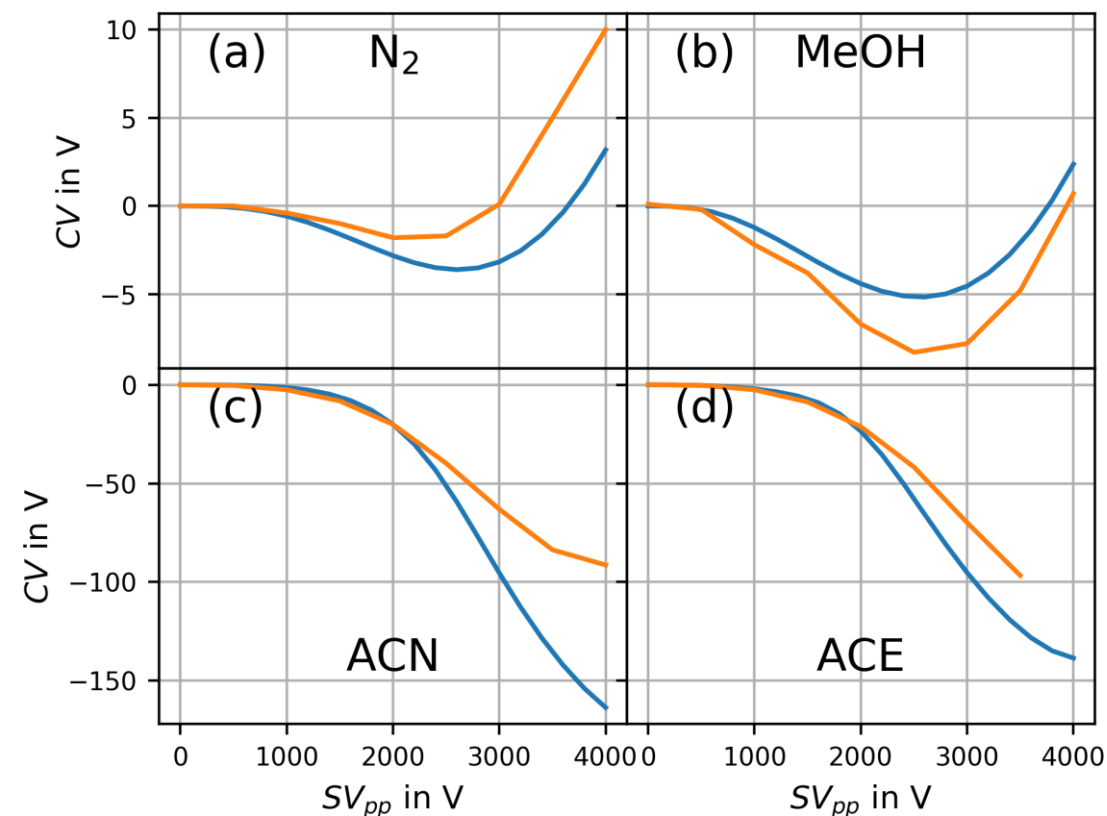
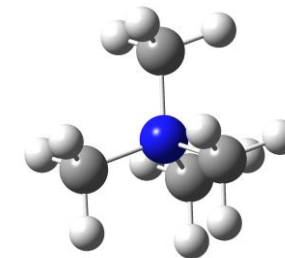
$$E(t) = \frac{D}{d} \cdot \left(\frac{2}{3} \sin(\omega t) + \frac{1}{3} \sin\left(2\omega t - \frac{\pi}{2}\right) \right)$$

$$SV_{pp} = \frac{3}{2} D$$

$$CV = - \frac{\langle \alpha(E(t)) \cdot E(t) \rangle_{wf}}{1 + \langle \alpha(E(t)) \rangle_{wf} + \langle \alpha'(E(t)) \cdot E(t) \rangle_{wf}} \cdot d$$



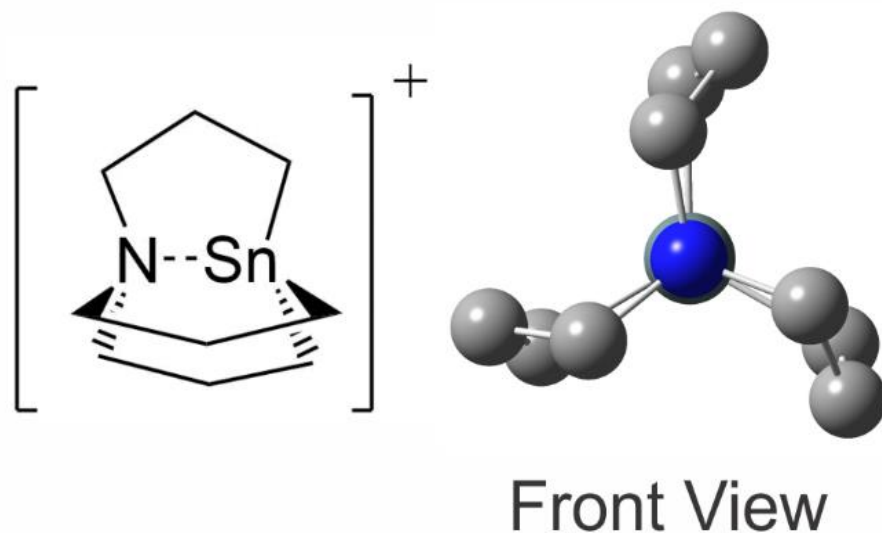
Int. J. Mass Spectrom. **128**, 143–148 (1993)
Int. J. Mass Spectrom. **285**, 149–156 (2009)



— experimental — calculated

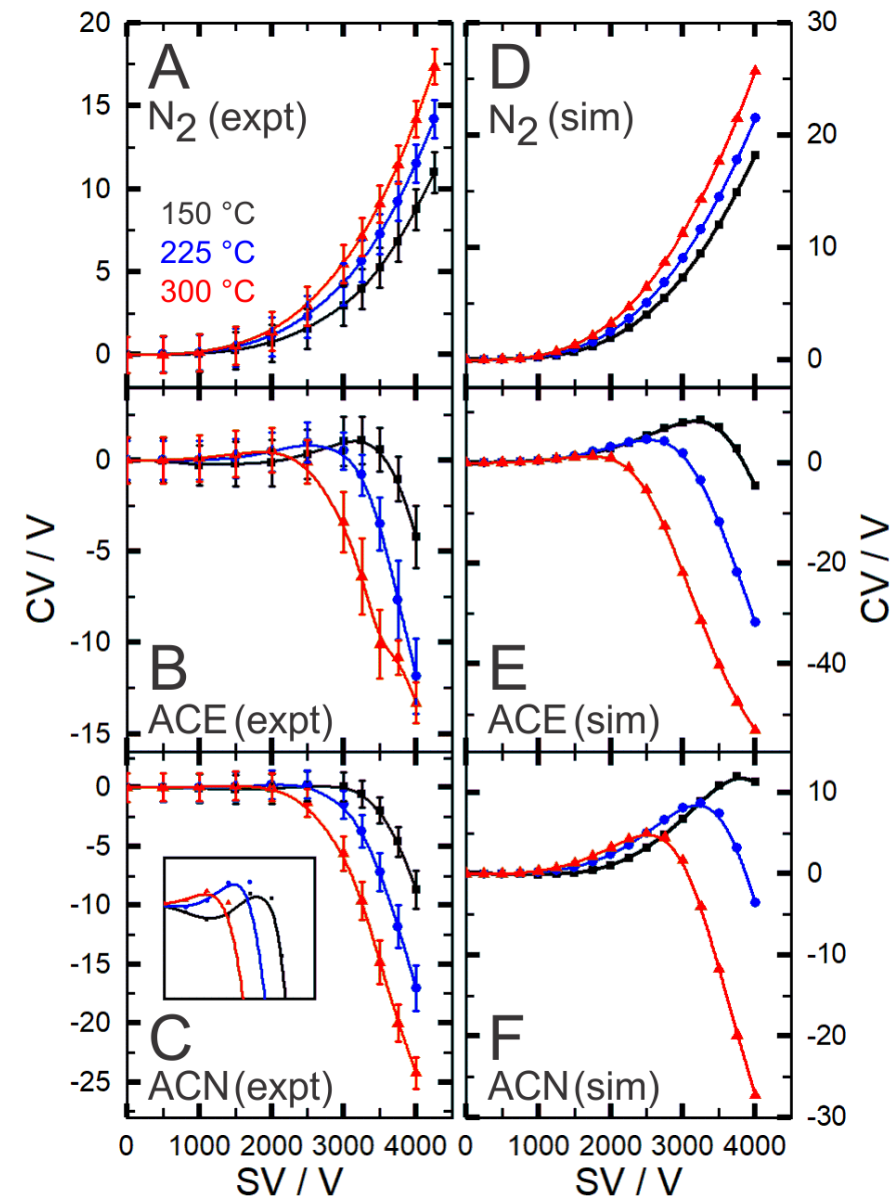
6.) DETERMINE DISPERSION PLOTS

- Type D dispersion plots: Tricarbastannatrane cation

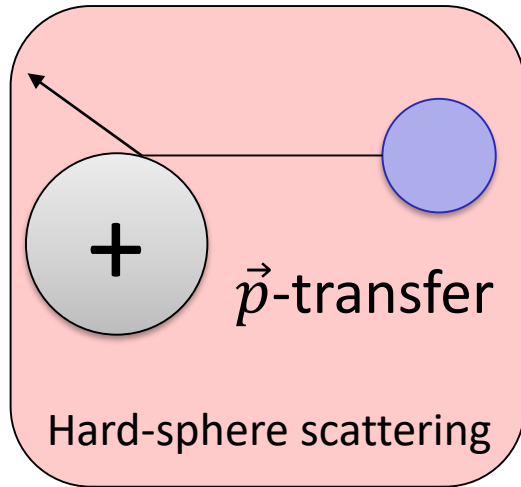


see Poster **10(b)**:

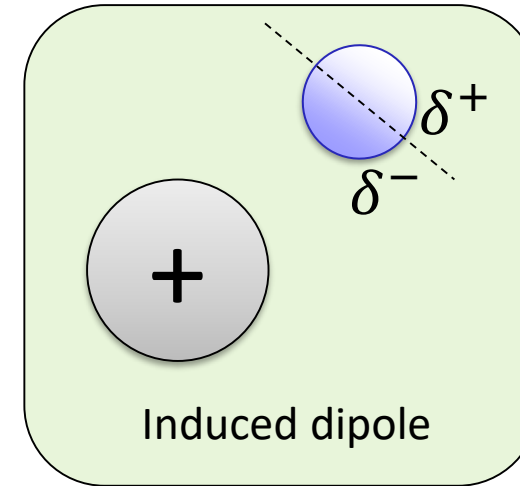
*Understanding non-traditional differential mobility behavior:
a case study of the tricarbastannatrane cation, $N(\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{Sn}^+$*



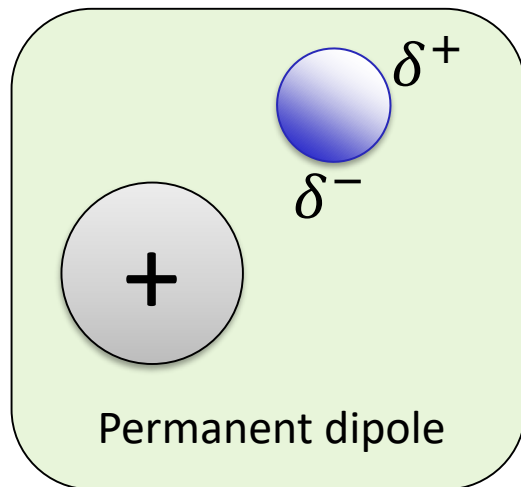
CONCLUSION



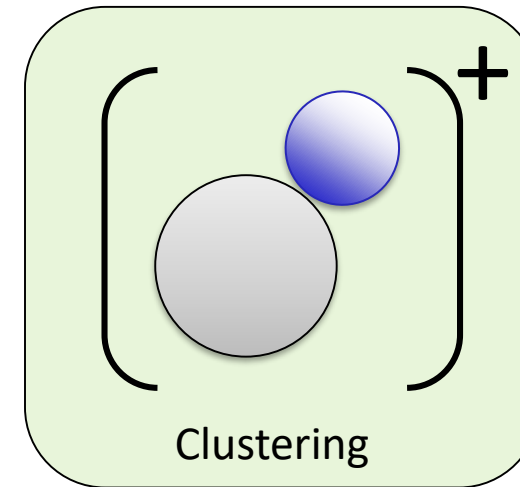
Use two-temperature theory



Correct modeling of $\Omega(T_{eff})$



?
Not incorporated yet



Correct modeling of cluster distribution, $P_i(E)$

ACKNOWLEDGEMENT



Physical and Theoretical
Chemistry



Prof. Scott Hopkins



DAAD

Deutscher Akademischer Austauschdienst
German Academic Exchange Service

Dr. Jeff Crouse

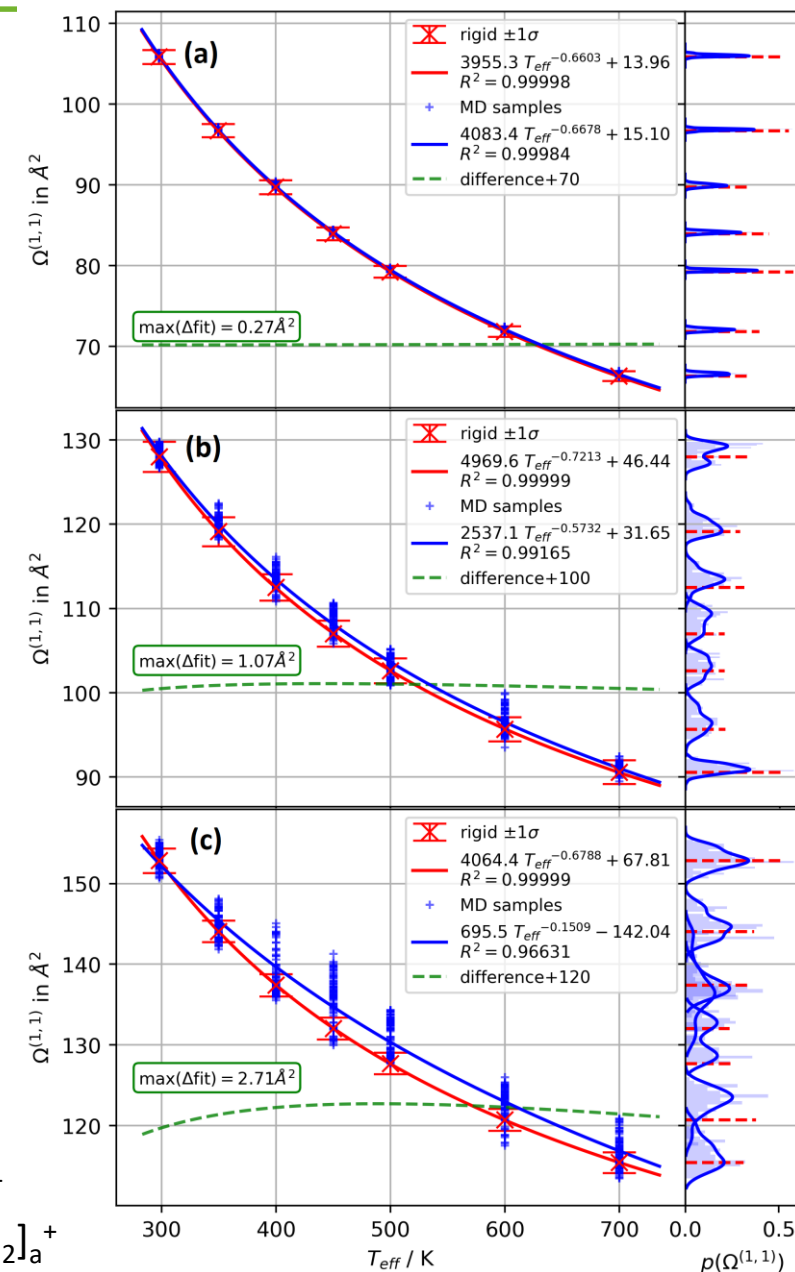
Christian Ieritano



QUESTIONS?

AND HOW DOES Ω CHANGE WITH T_{eff} ?

- CCS is function of (effective) temperature
 - Relative velocity distribution changes (included in MobCalc-MPI)
 - Internal energy and thus vibrational broadening increases
- Calc CCS at different temperatures for
 - Rigid equilibrium structure
 - 100 sample geometries from a MD simulation at that temperature
- Fit the data to $\Omega(T_{eff}) = a \cdot T_{eff}^b + c$
- For stiff molecules, fitting functions are the same
- For floppy ones, differences might be significant



(a) Me_4N^+
 (b) $[\text{Me}_4\text{N}+\text{ACE}]^+$
 (c) $[\text{Me}_4\text{N}+(\text{ACE})_2]_a^+$

HOW MUCH IS THERE OF EACH CLUSTER?

- So far, harmonic-superposition approximation used
 - Assumes equilibrium for the given field strength E
 - Can be computed from First Principles

$$Z_i = \left(\frac{[M]}{N} \right)^{n_i} Q_i(T_{eff}) \exp \left(- \frac{\varepsilon_n - \varepsilon_{ref}}{k_B T} \right)$$

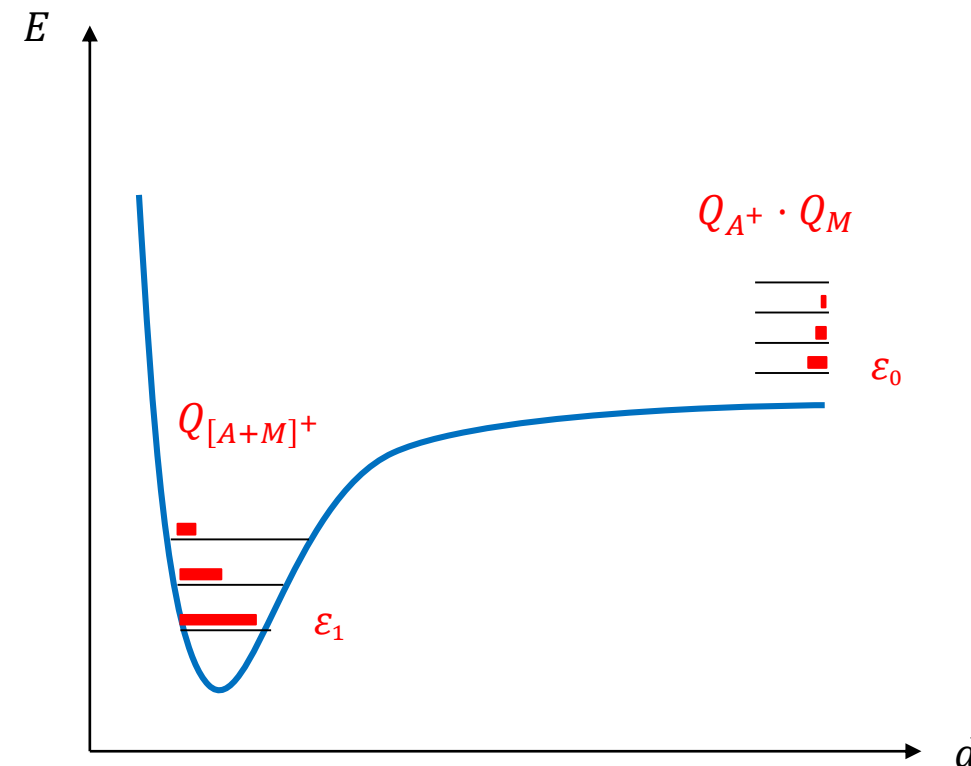
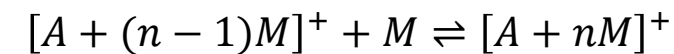
???

$$P_i = \frac{Z_i}{\sum_i Z_i}$$

$$Q_i(T_{eff}) = Q_{[A+n_iM]^+}(T_{eff}) \cdot Q_M(T)^{n_{max}-n_i}$$

$$\varepsilon_i = [\varepsilon_{elec} + \varepsilon_{ZPE}]_{[A+n_iM]^+} + (n_{max} - n_i)[\varepsilon_{elec} + \varepsilon_{ZPE}]_M$$

$$K(E) = \sum_i P_i(E) \cdot K_i$$



HOW MUCH IS THERE OF EACH CLUSTER?

- Think about $A \rightleftharpoons B$ where $T_A = T_B$
- Superposition approximation:

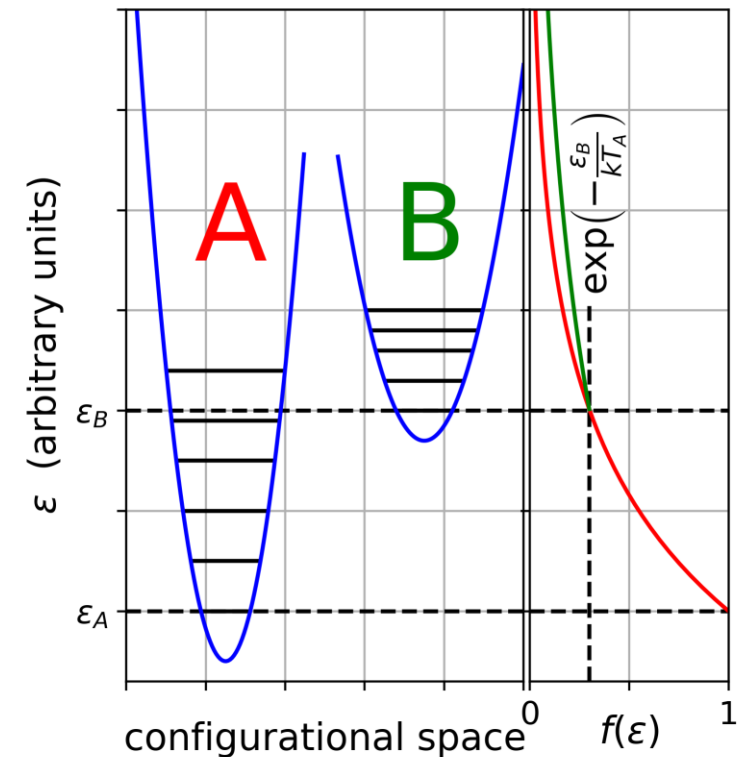
$$Z = Z_A + Z_B = \underbrace{\int_{\varepsilon_A=0}^{\infty} \rho_A(\varepsilon) \exp\left(-\frac{\varepsilon}{kT}\right) d\varepsilon}_{= Q_A(T)} + \int_{\varepsilon_B}^{\infty} \rho_B(\varepsilon) \exp\left(-\frac{\varepsilon}{kT}\right) d\varepsilon$$

$$Z_B = \exp\left(-\frac{\varepsilon_B}{kT}\right) \int_{\varepsilon_B}^{\infty} \rho_B(\varepsilon) \exp\left(-\frac{\varepsilon - \varepsilon_B}{kT}\right) d\varepsilon = \exp\left(-\frac{\varepsilon_B}{kT}\right) \underbrace{\int_0^{\infty} \rho_B(\tilde{\varepsilon}) \exp\left(-\frac{\tilde{\varepsilon}}{kT}\right) d\tilde{\varepsilon}}_{= Q_B(T)}$$

$$Z = Z_A + Z_B = Q_A(T) + Q_B(T) \exp\left(-\frac{\varepsilon_B}{kT}\right)$$

$$\xrightarrow{T_A \neq T_B} Z = Z_A + Z_B = Q_A(T_A) + Q_B(T_B) \exp\left(-\frac{\varepsilon_B}{kT_A}\right)$$

$$P_i = \frac{Z_i}{\sum_i Z_i}$$



HOW MUCH IS THERE OF EACH CLUSTER?

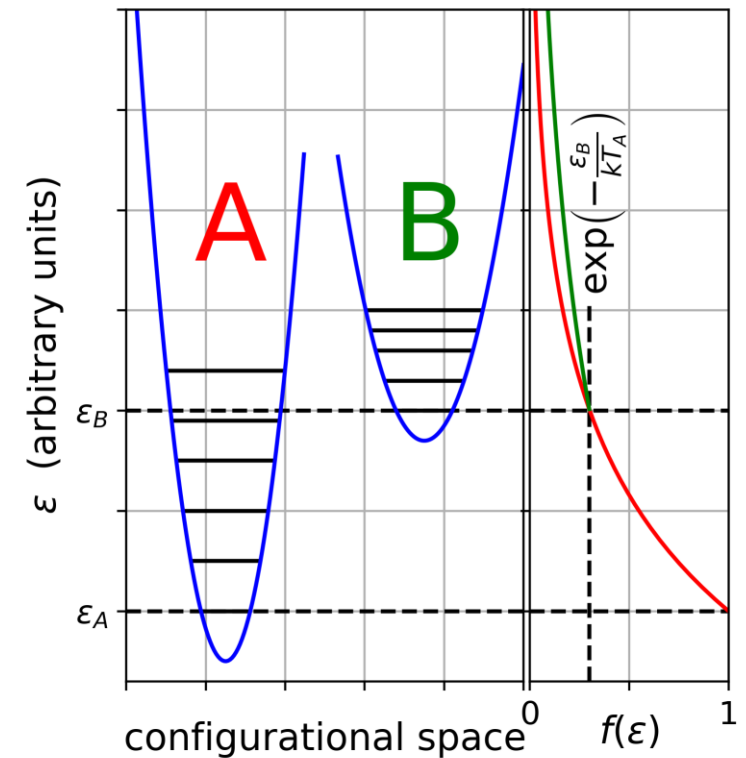
- For energy sorted minima (i.e. $\varepsilon_{i+1} > \varepsilon_i$)
- Weight Q_i with *all* scaling factors which have $j < i$

$$Z_1 = \left(\frac{[M]}{N}\right)^{n_1} Q_1(T_1) Q_M(T)^{\tilde{n}-n_1}$$

$$Z_i = \left(\frac{[M]}{N}\right)^{n_i} Q_i(T_i) Q_M(T)^{\tilde{n}-n_i} \cdot \exp\left(-\sum_{j=2}^i \frac{\varepsilon_{0,j} - \varepsilon_{0,j-1}}{k_B T_{j-1}}\right) \quad \text{for } i \geq 2$$

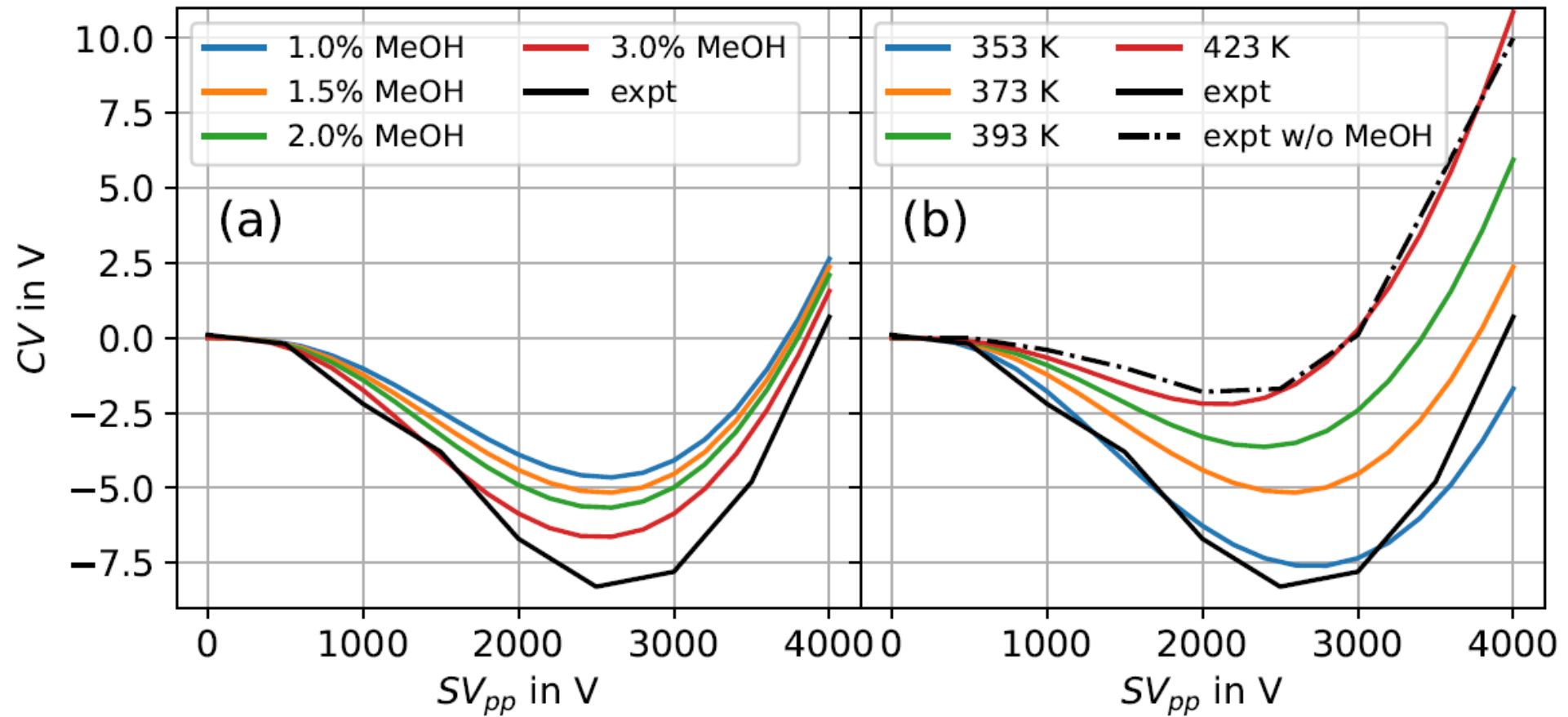
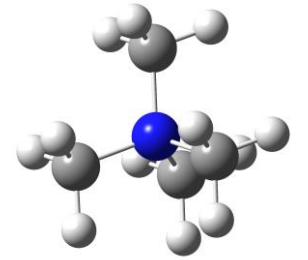
- Reduces back to normal superposition approx. if all T_i are equal

$$P_i = \frac{Z_i}{\sum_i Z_i}$$



6.) DETERMINE DISPERSION PLOTS

- Variation of modifier concentration and temperature





DISCUSSION

Problem	Solvable?	Ideas	Literature
Two-temperature theory is only an approximation	Yes	Include higher order terms, or use momentum-transfer theory	<i>Anal. Chem.</i> 84 (22), 9782-9791 (2012) <i>Analyst</i> 141 (23), 6396-6407 (2016)
Vibrational broadening and inelastic collisions are neglected	Yes	Perform actual MD simulations for CCS determination	IMoS 2.0 <i>J. Chem. Phys.</i> 148 (6), 064109 (2018)
Equilibrium at all time assumed (might not hold for fast varying fields)	Yes	Instead of (weird) superposition approximation, calculate rate constants (RRKM theory) and perform actual kinetic computations	MultiWell <i>J. Chem. Phys.</i> 106 (11), 4499-4508 (1997) <i>J. Am. Soc. Mass Spectrom.</i> 8 (2), 103-115 (1997)
Contribution of solvent molecules (1.5% v/v) to CCS are neglected	Yes	Either modify MobCal-MPI or perform MD simulations for CCS determination including the solvents	
Partition functions are calculated with standard approximations (rough approx. for anharmonic clusters)	Yes	Perform anharmonic correction calculations (VPT2) Or use Quasi-Harmonic approximation (MD simulations have to be performed; can be used for CCS calcs as well)	<i>J. Chem. Theory Comput.</i> 8 (3), 1015-1036 (2012) <i>J. Chem. Theory Comput.</i> 12 (12), 5990-6000 (2016)
Account for coupling of all effects with reasonable effort	No	... when was life ever easy?	