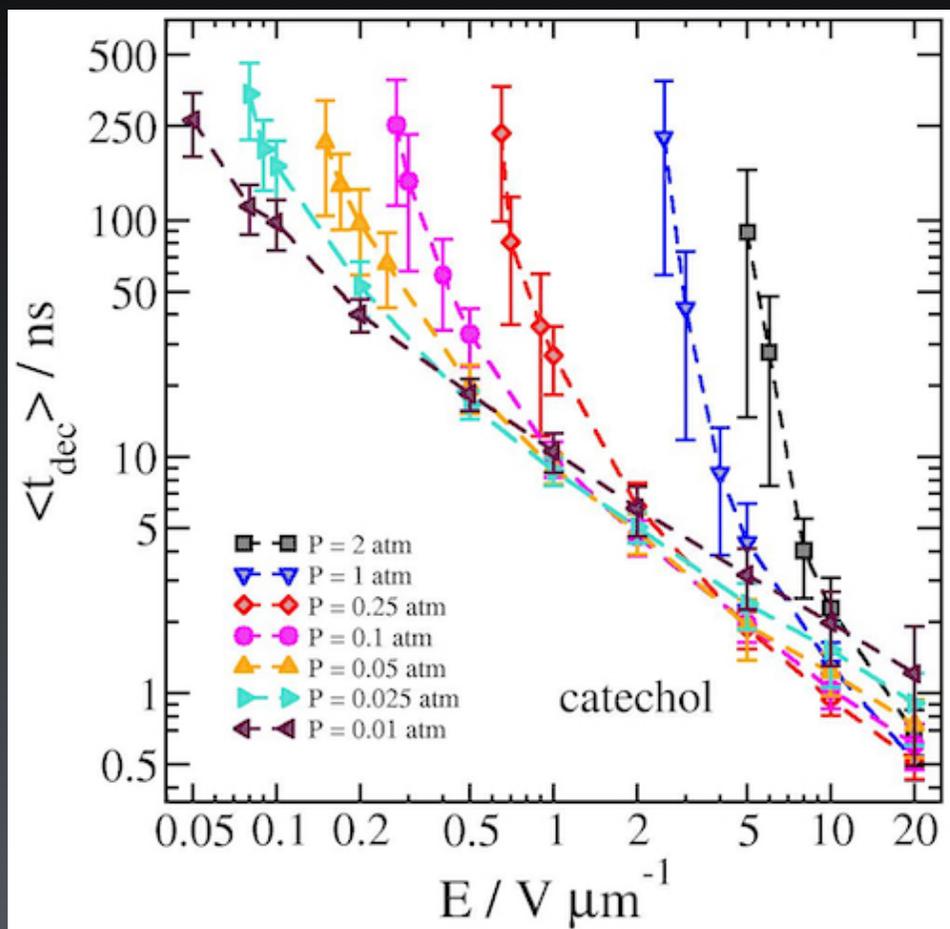


Molecular dynamics simulations as probes of the decomposition kinetics of atmospheric molecular complexes: A case study of nitrate chemical ionization

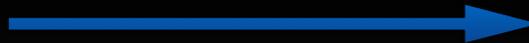


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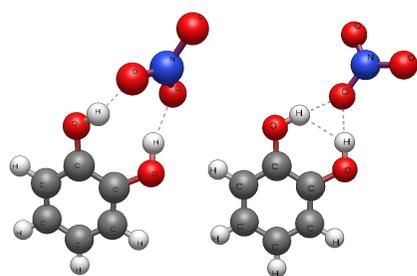


- As a bridge between working for Theo and working for Matti, we tried to find a nice MD project of interest.
- We thought it would be worth doing MD on a straightforward system amenable to empirical force-field-based methods, that is, nitrate ion complexes with various atmospheric molecules. These are a key component of the nitrate-CIMS instruments Matti's group uses (and many others!).

- We use force fields based on the OPLS framework, with several modifications (eg. increased partial charges on the nitrate ion).
- The empirical force field matches quantum chemistry for binding energy within 2-3 kcal/mol and the cluster minima mostly look similar to the DFT-optimized minima. Good enough!
- Systems studied are shown here, they include 3 related diphenols, nitrophenol and also $\text{HNO}_3 \cdot \text{NO}_3^-$ since this cluster is an important species in the ionization region of nitrate CIMS.

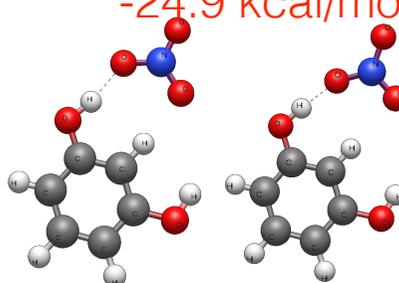
ΔE_{bind}

-27.3 kcal/mol

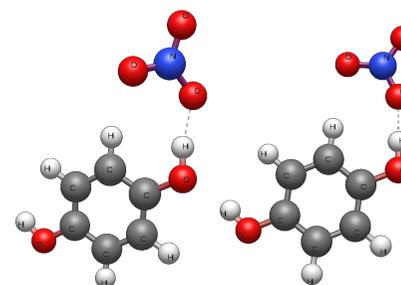


catechol · NO_3^-

-24.9 kcal/mol



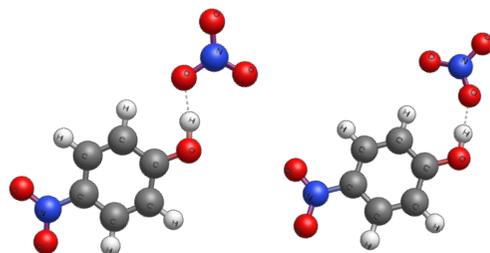
resorcinol · NO_3^-



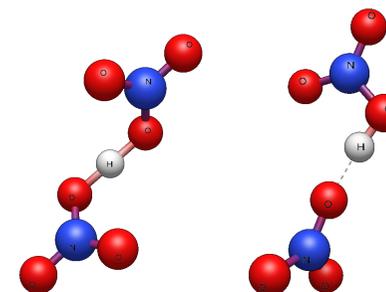
hydroquinone · NO_3^-

-20.3 kcal/mol

-29.3 kcal/mol



4 - nitrophenol · NO_3^-



$\text{HNO}_3 \cdot \text{NO}_3^-$

-29.4 kcal/mol

1) Cluster decomposition in vacuo:

- Start from global minimum optimized structure for each cluster.
- Run ~1000 simulations at each different initial T
- Compute survival probability $P(t)$ for the cluster to stay together. Then eg. $-dP/dt$ is a rate for cluster decomposition (or do more involved modelling).

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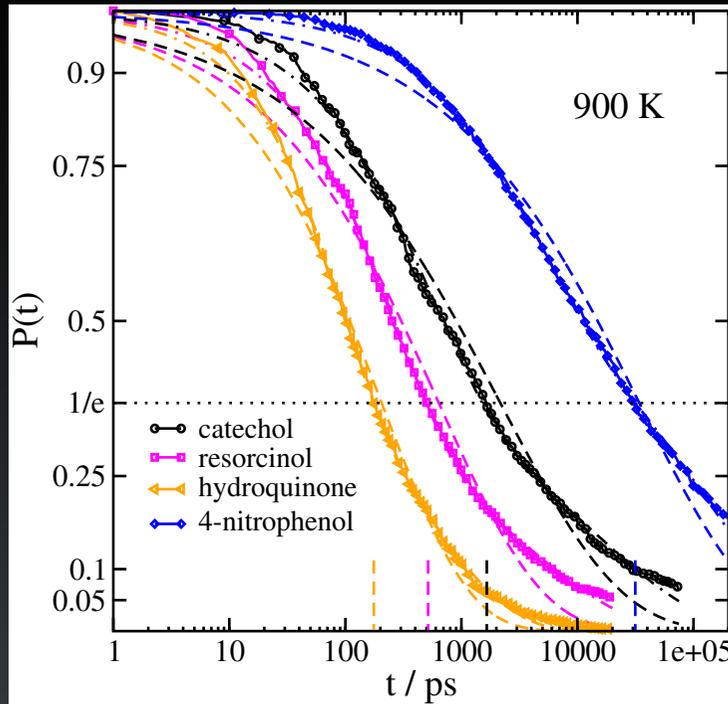
- Put each cluster in N_2 gas with different pressures
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2) Add Electric field:

- Electric field accelerates the charged cluster through the gas.
- Does it break up differently vs. the pure thermal decomposition?

1) Decomposition in vacuo:

(Note elevated temperature)



A simple exponential does not work! There is a very long tail, some clusters remain bound for a very long time.

Instead, I am using (a) stretched exponential(s) to model the survival probability:

$$P_{s1}(t) = \exp(- (t/\tau)^\beta)$$

sum of 2 also useful, 5 parameter fit:

$$P_{s2}(t) = \frac{1}{1 + A_2} \left[e^{-(t/\tau_1)^{\beta_1}} + A_2 e^{-(t/\tau_2)^{\beta_2}} \right]$$

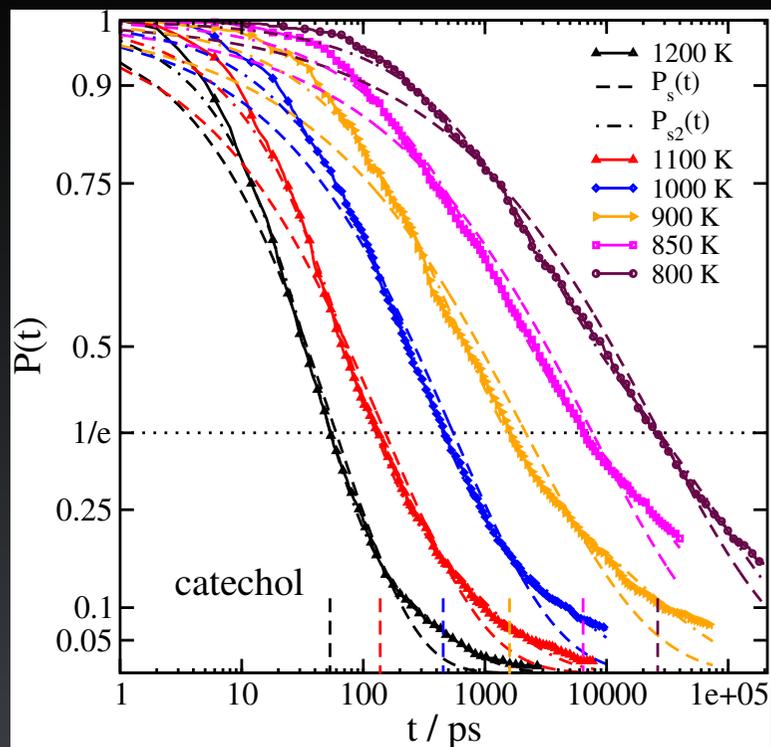
Mean relaxation time is the integral of P(t):

$$\langle \tau \rangle = \int_0^\infty P(t) dt$$

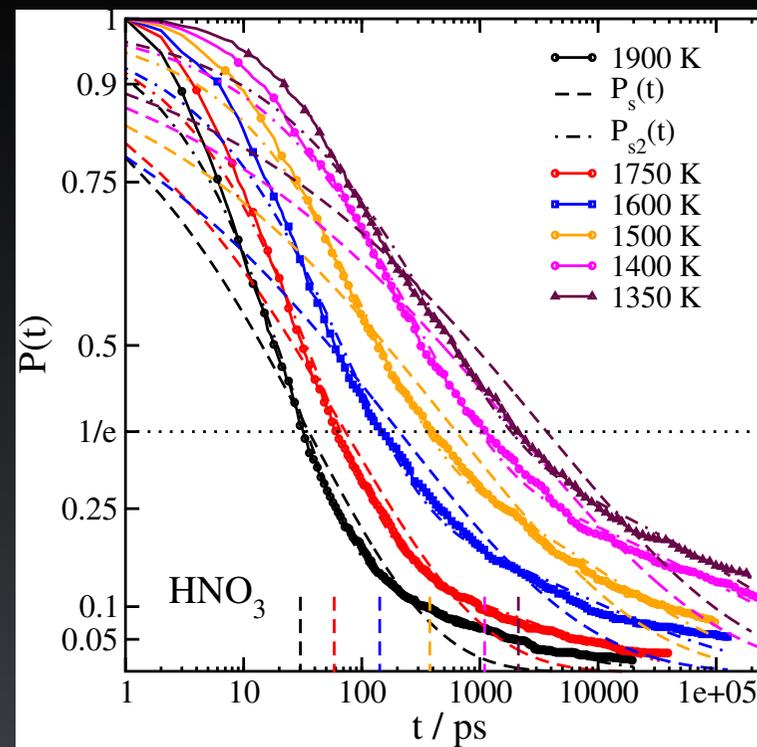
If $P(t) = \exp(-t/\tau)$, $\langle \tau \rangle = \tau$

$$\langle \tau_{s2} \rangle = \frac{1}{1 + A_2} \frac{\tau_1}{\beta_1} \Gamma\left(\frac{1}{\beta_1}\right) + \frac{A_2}{1 + A_2} \frac{\tau_2}{\beta_2} \Gamma\left(\frac{1}{\beta_2}\right)$$

catechol + NO_3^-

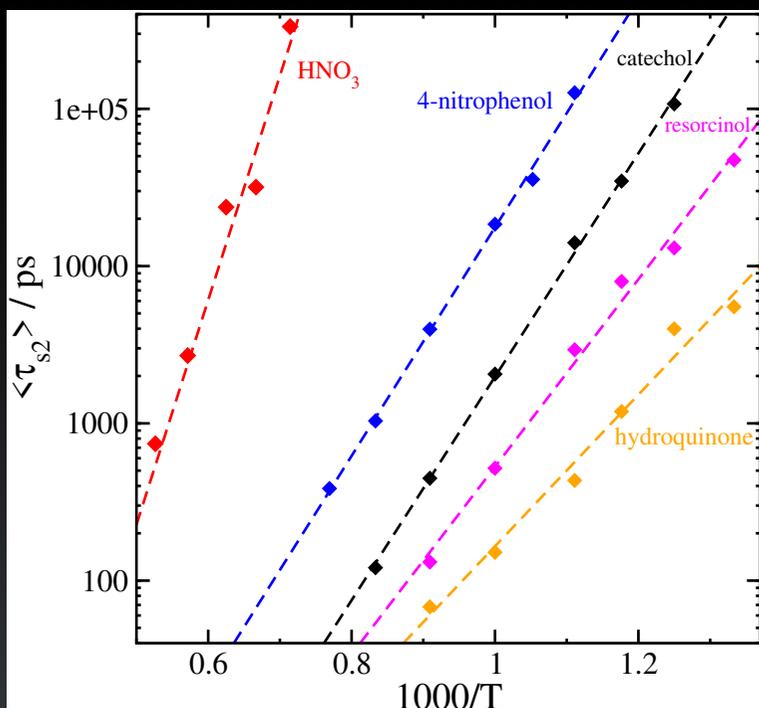


HNO_3 + NO_3^-



Raw data in solid lines, fits are in dashed/dash-dotted lines.

There can be issues at lower T , since impossibly long runs are needed to get the long tail. So it could be that fits at lower T underestimate $\langle \tau \rangle$ and overestimate β . Especially for nitric acid case.



If we have some kind of Arrhenius behaviour, then $\log\langle\tau\rangle$ vs. $1/T$ should be linear: $\langle\tau_{s_2}\rangle(T) = A\exp(B/k_B T)$

Looks pretty good! Extrapolating to 300 K, I would predict:

	A/fs	B/kcal mol ⁻¹	extrapolated $\langle\tau\rangle$
catechol	0.155	32.51	870 days
resorcinol	0.574	27.29	12.1 hours
hydroquinone	2.50	22.09	29 s
4-nitrophenol	9.61	33.23	~500 years
nitric acid	0.017	65.28	~10 ²³ years

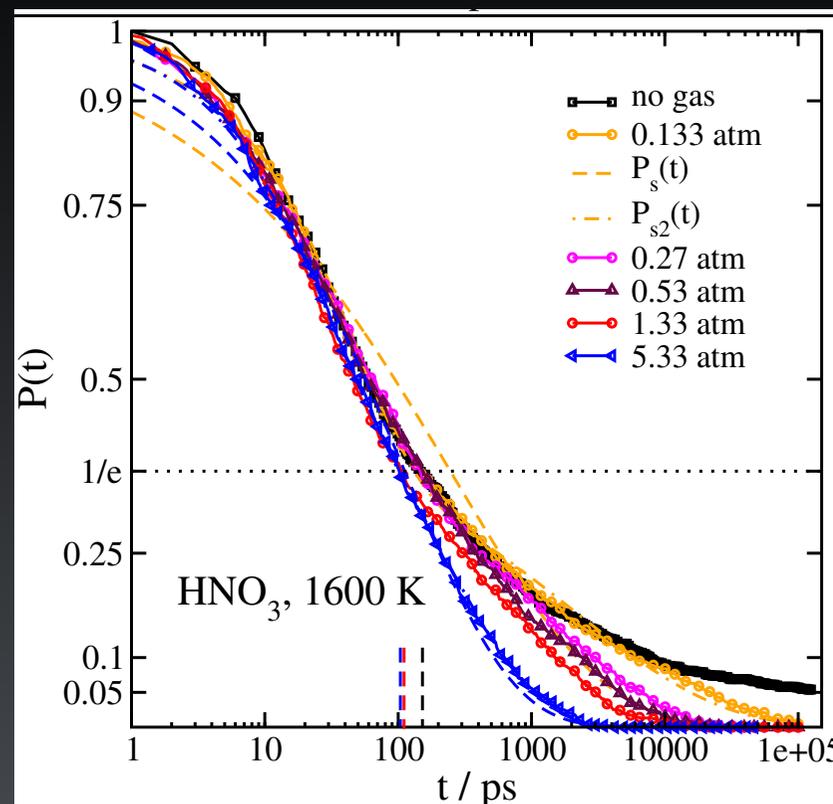
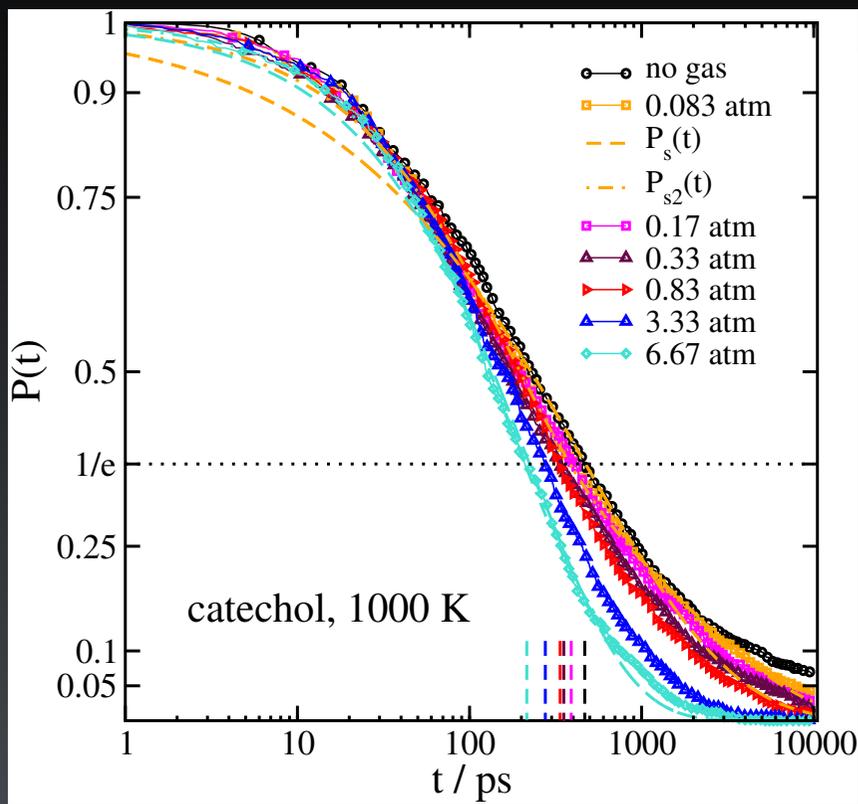
Empirically at least, this fits the expected trend based on binding energies.

- No comparison to experiment (yet)... but we can compare to dissociation rates γ from detailed balance (Vehkämäki et al.)
- We predict much lower dissociation rates! The long-tailed distribution again... (also probably other issues, too much extrapolation etc.)

	detailed balance, 300K	$1/\langle\tau\rangle$, 300K	detailed balance, 900/1600K	$1/\langle\tau\rangle$, 900/1600K
catechol	0.02 /s	1.33×10^{-8}	2.28×10^{12}	4.87×10^8
nitric acid	7.43×10^{-6} /s	1.65×10^{-31}	3.94×10^{13}	4.22×10^7

1a) Add some gas:

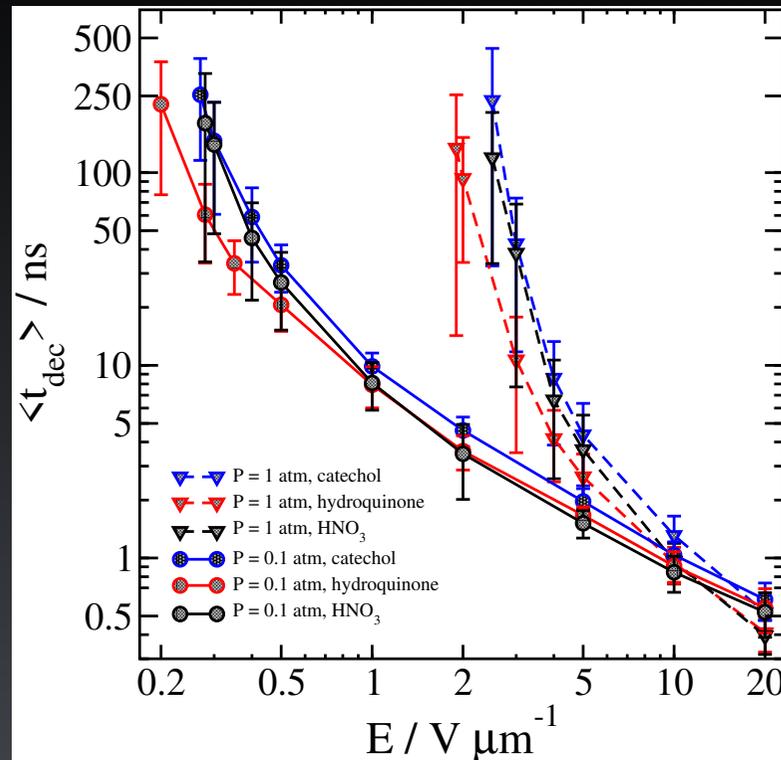
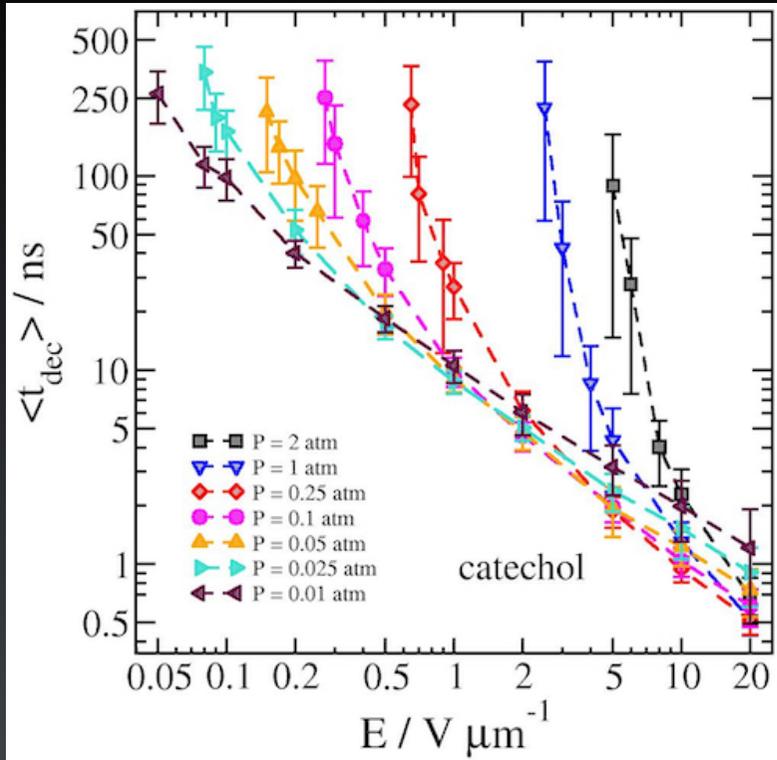
In a gas the clusters get thermalized better, so those long tails are less long



Especially the smaller HNO_3 cluster!

- The gas will effectively reduce the cluster lifetimes by at least an order of magnitude, and much more in some cases.
- But not enough to completely explain the different predictions of dissociation rates.

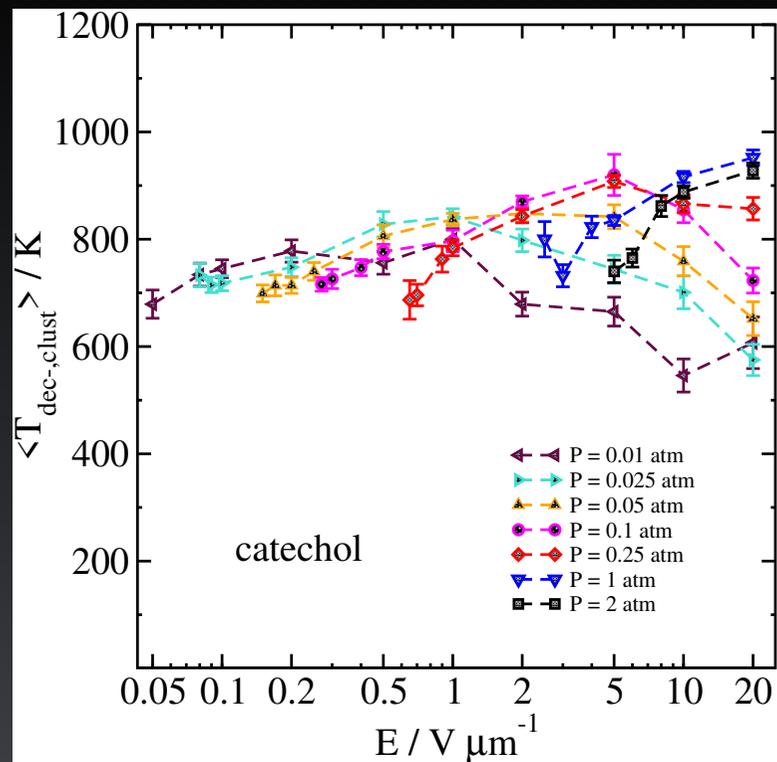
2) Add Electric field:



Nitric acid cluster accelerates faster, so decomposes a bit faster than other clusters.

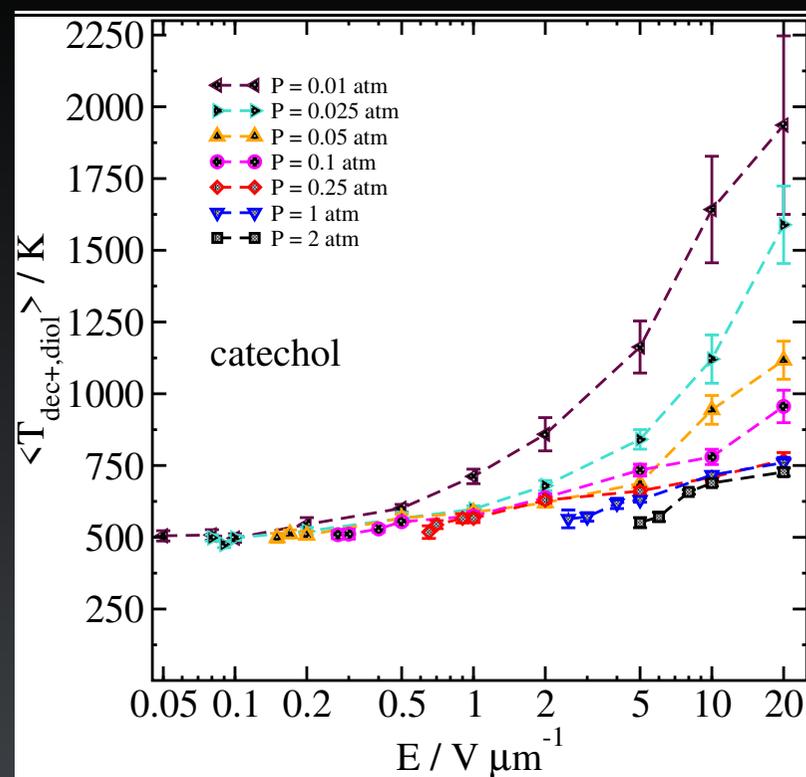
- Starting $T=300$ K. Average of ~ 100 runs.
- Higher field strength accelerates the charged cluster faster, so it decomposes sooner.
- In lower field, higher pressure makes a difference since the cluster's acceleration slows due to drag.
- In high field, the cluster moves so fast and collisions are so energetic that pressure dependence seems to go away (or cancel out).

Cluster T, 2ps before decomposition



- Weak increase with field
- But at low P + high $|E|$, T_{clust} just before decomposition is lower! Not just thermal, ie. a single collision with the gas can cause the decomposition.

Molecule T, just after decomposition



- Similarly, temperature of the molecule just after decomposition is lower in low field...
- ... but higher in high field!

Take-home messages

- This work uses molecular dynamics to simulate cluster decomposition directly. Surprisingly doesn't seem to have been done before!
- MD simulations show that cluster/complex lifetimes have a very broad distribution.
- **An isolated cluster in vacuum does not have a well-defined temperature! So individual clusters might last longer than expected if they are cold, and these are what show up in the long tail.**
- This is especially important for smaller molecules with less degrees of freedom.
- Effect of collisions with gas is important, but timescale for gas to thermalize the clusters may still be long compared to cluster lifetime in some cases
- In high field/low pressure, thermalization is incomplete and high-energy collisions directly cause decomposition.
- More thought is required!

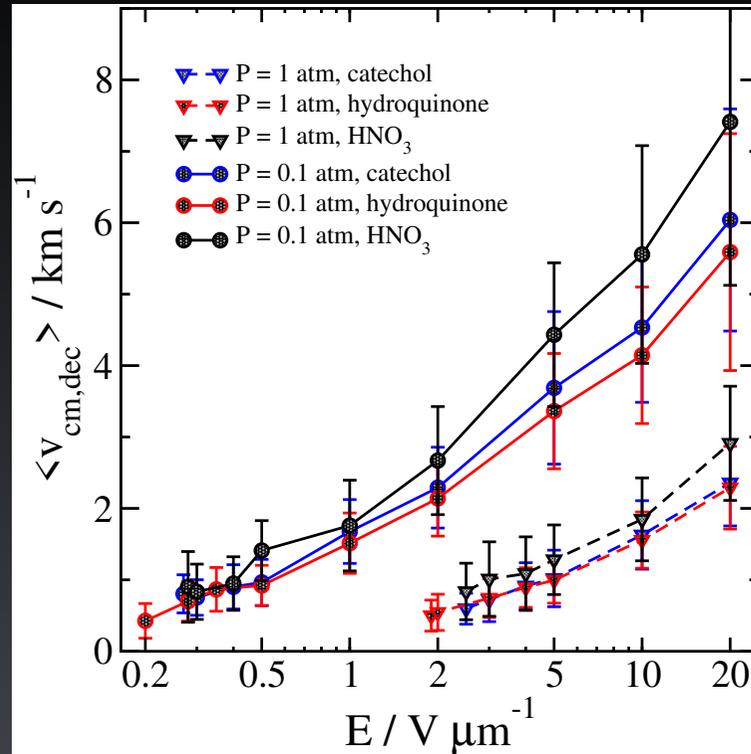
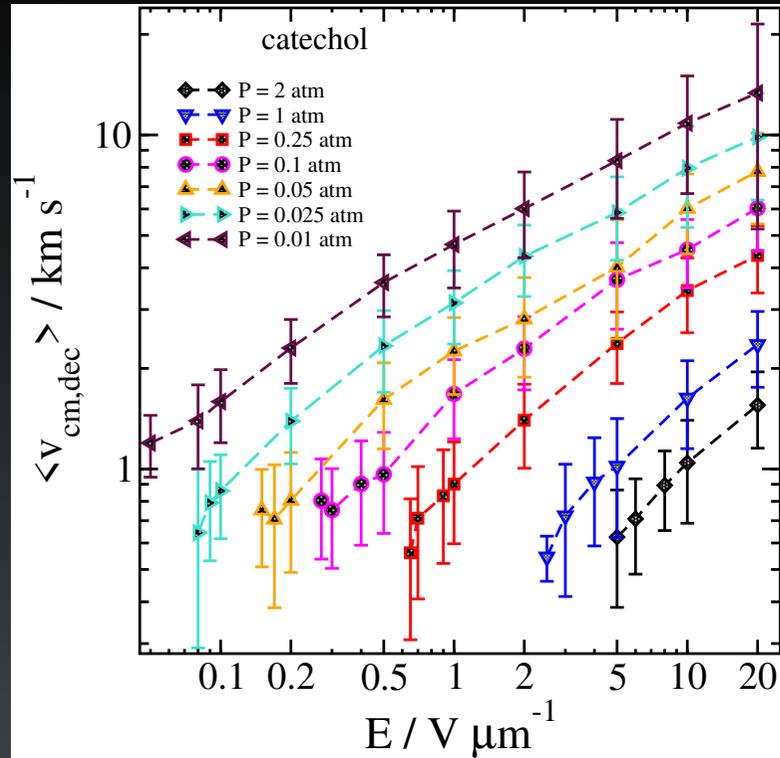
Future plans:

- Think more about the comparison with detailed balance: maybe run simulations on less strongly bound clusters?
- **Try to figure out how to compare these results directly with experimental data.**

~~Paper will be in PCCP real soon!~~

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Velocity at decomposition, you can see the drag playing a role.



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