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Technology
Facilities Council

Scientific Computing

HPC Applications in Materials

Alin M Elena

computational materials and molecular sciences



Data-driven Materials
and Molecular Science

July 3, 2025



CCP5
Collaborative
Computational Project
Computer Simulation of Condensed Phases

CoSeC

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PSDI
PHYSICAL SCIENCES
DATA INFRASTRUCTURE



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Swindon

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Observatory





agenda

introduction
HF dissociation in water clusters by
computer simulations
conclusions

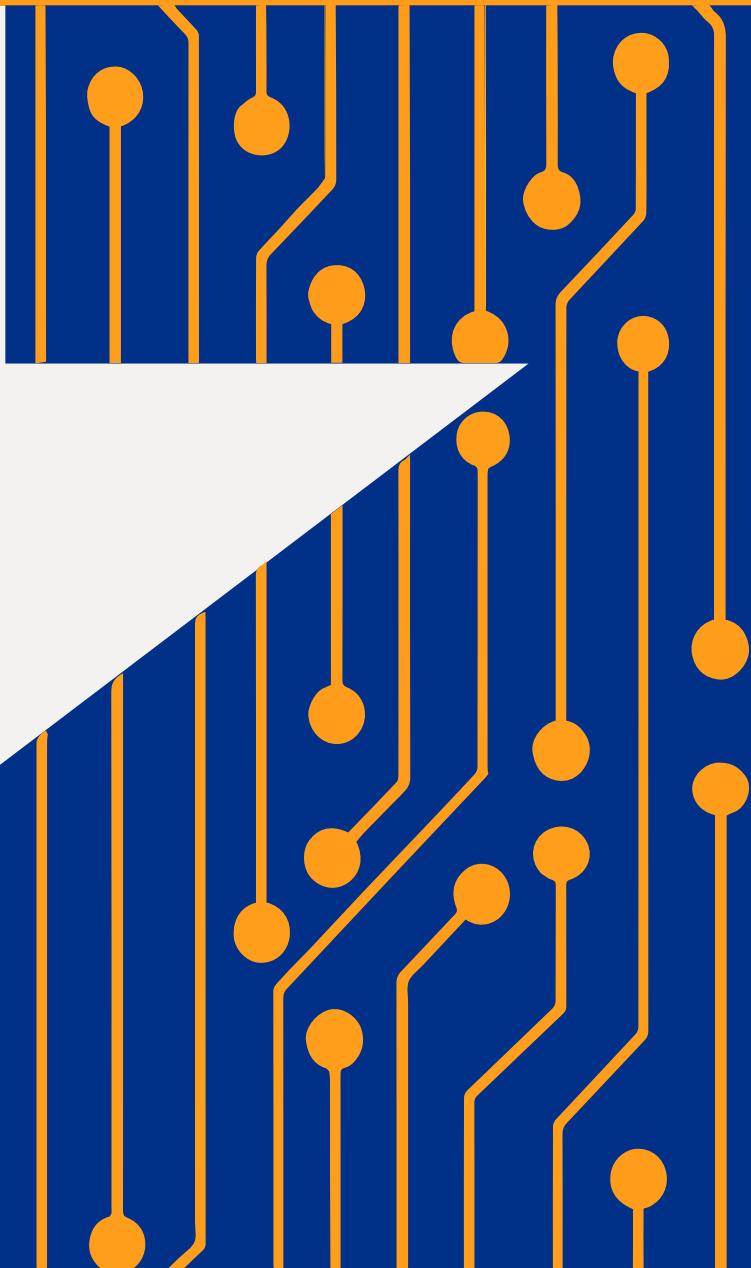




introduction

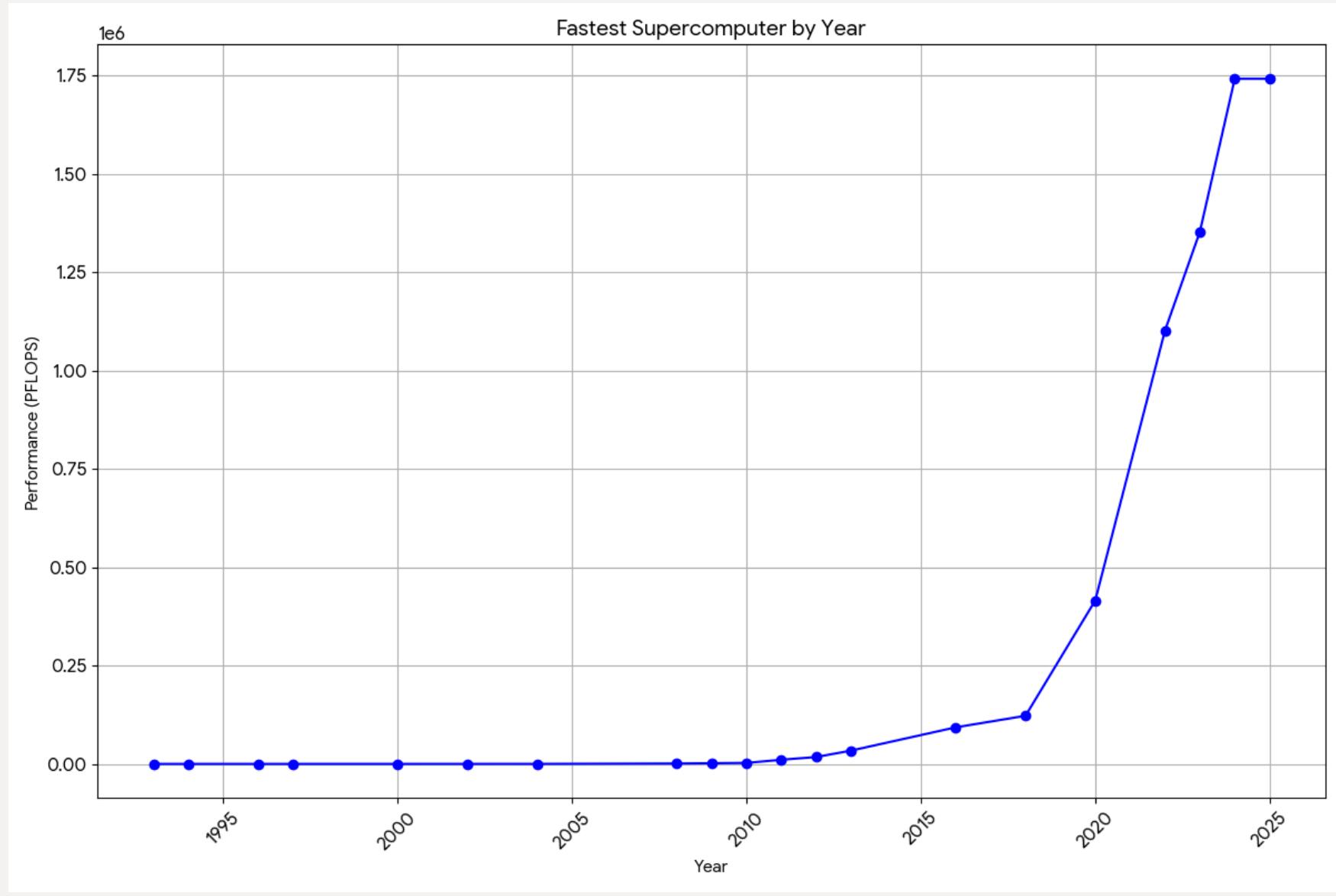
HF dissociation in water clusters by
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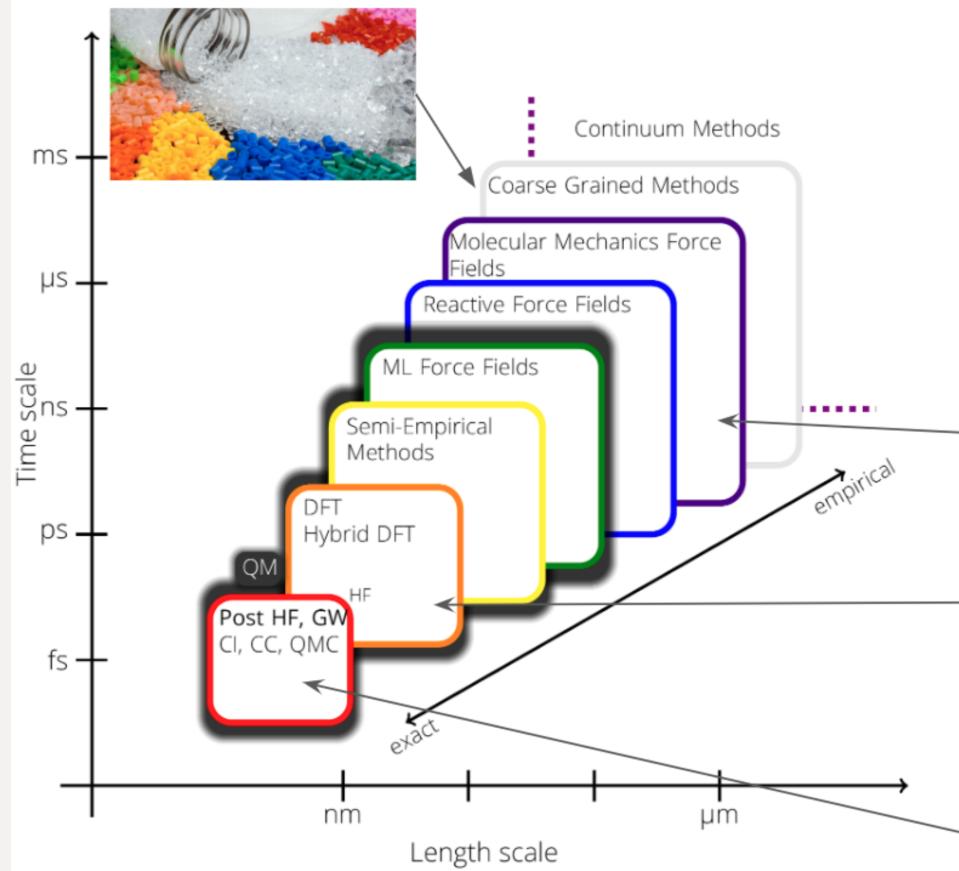
Petaflops



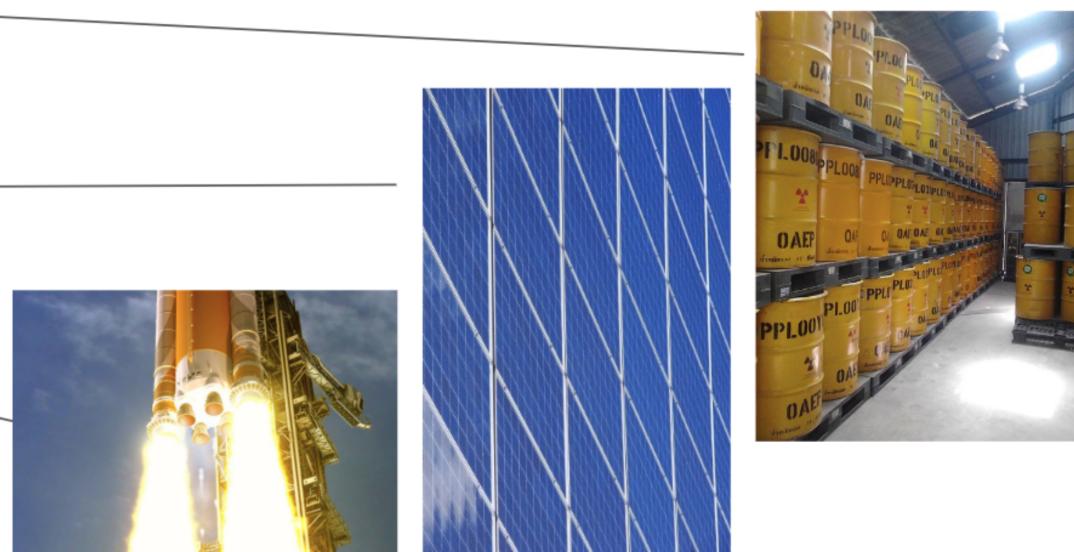
Modelling



Materials sciences



Method	Complexity	Typical performance
Coarse Grained/MD	$O(N \log N)$	1-10s TFlops
ML FF	$O(N \log N)$	10s TFlops
Semi DFT/HF	$kO(N)-O(N^2)$	10s-100 TFlops
DFT/HF	$kO(N)-O(N^4)$	10s TFlops-1 PFlop
GW	$O(N^{3-4})$	10s PFlops
CC	$O(N^{5+})$	
CI	$O(N^x)-O(N!)$	----

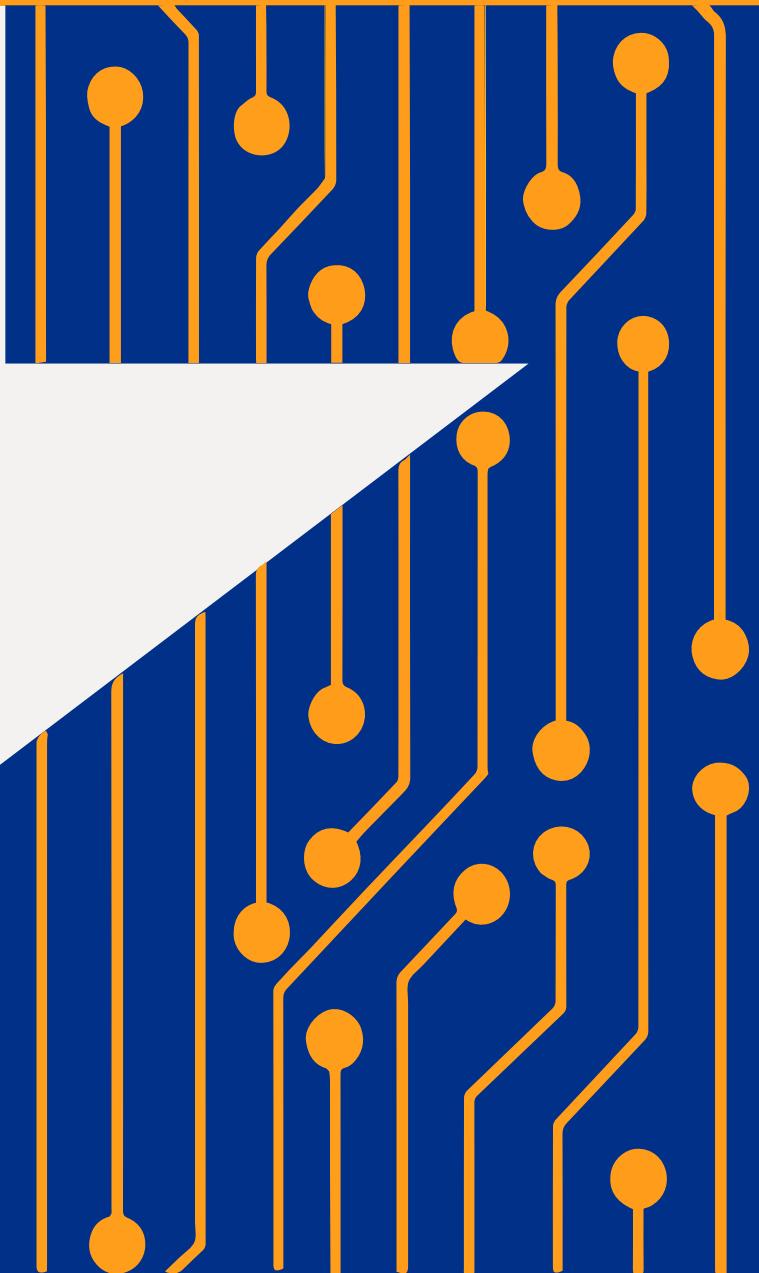




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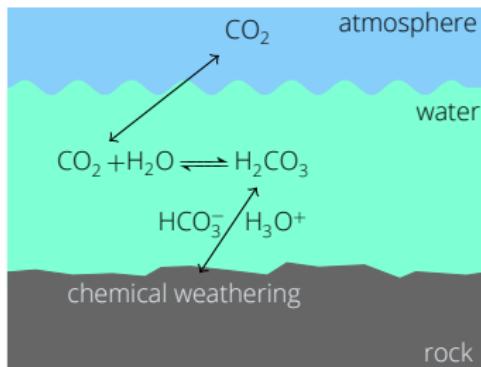
Outline

- 1 Motivation
- 2 Methods Developed and Used
 - Collective Variables
 - Restrained hybrid Monte Carlo
 - Rate Constant Calculation
- 3 Results
 - Collective Variable
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 - Equilibrium Constant
 - Mechanism of the Reaction
 - Reaction Rate Constant

Acid dissociation



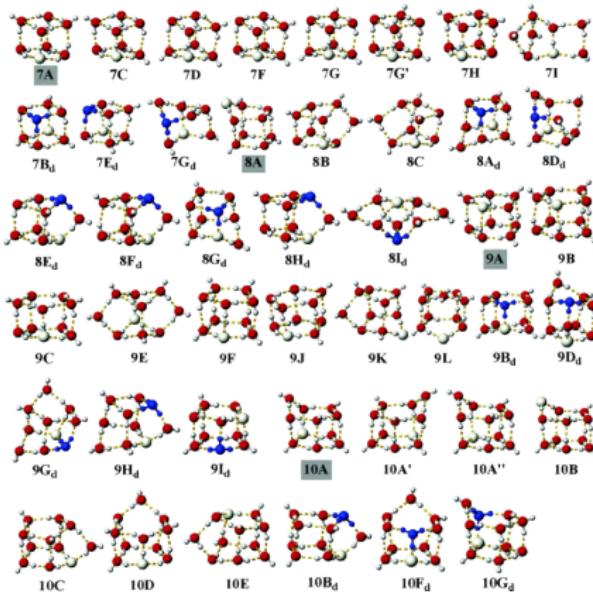
carbon cycle



biological systems



HF dissociation

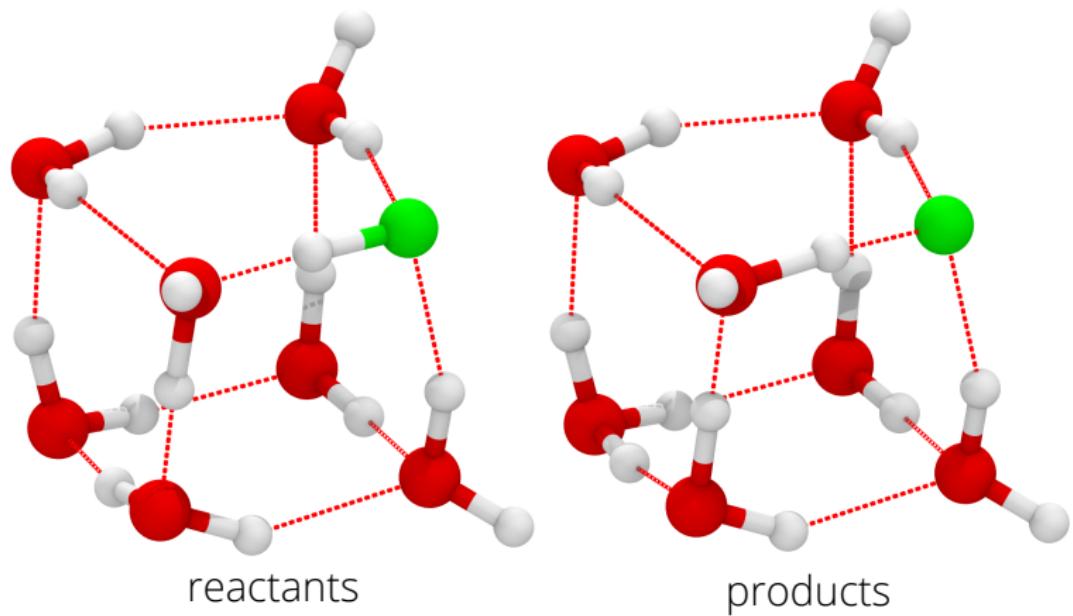


- Atmospheric chemistry, pockets in proteins...
- Testing ground for development of models for dissociation reaction in bulk

P. Ayotte, M. Hébert & P. Marchand, *J. Chem. Phys.* 2005, **125**, p. 184501

S. Odde et al., *J. Phys. Chem. A*, 2006, **110**, p. 7918

Dissociation of HF in $\text{HF}(\text{H}_2\text{O})_7$



Objectives

- Equilibrium constant
- Reaction mechanism
- Reaction rate constant

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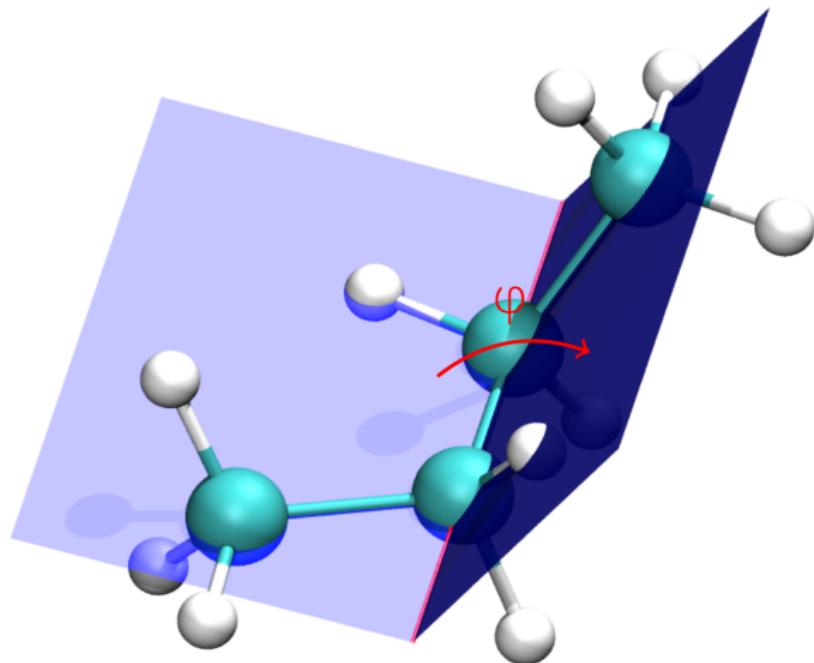
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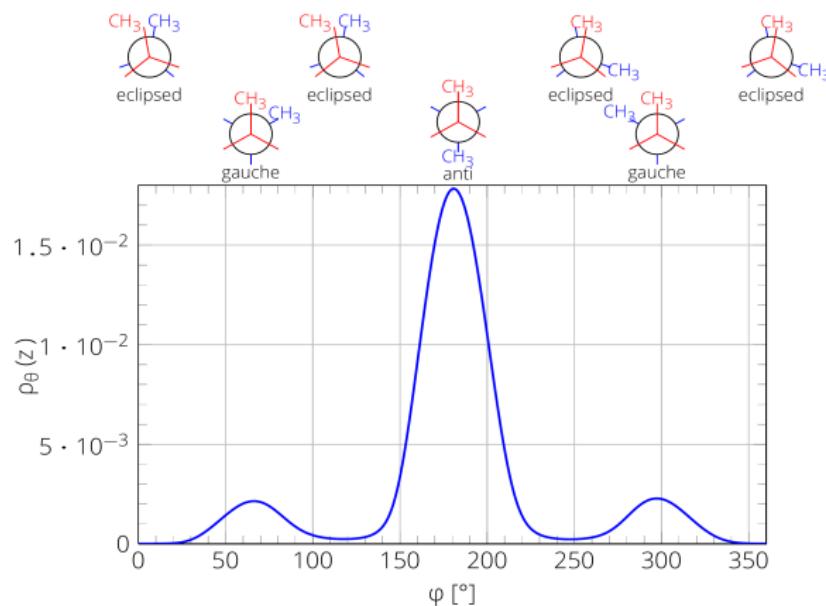
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Description of a process by collective variables I



Description of a process by collective variables II



Description of a process by collective variables III

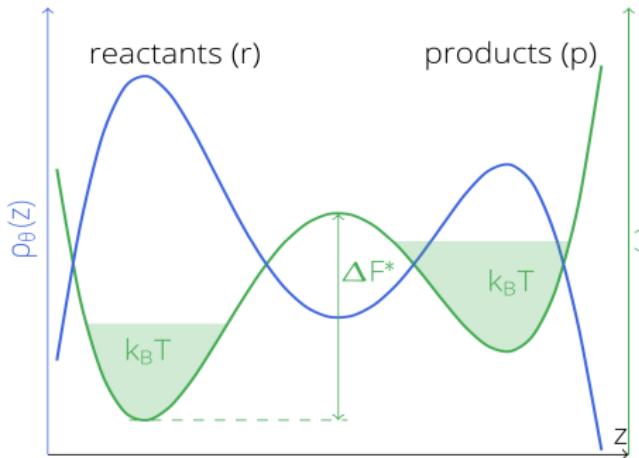
- collective variables(CV) microscopic observables that describe the process of interest, eg. chemical reaction
- order parameters: CVs that distinguish between initial and final state
- reaction coordinates CVs that describe the process along its path

mathematically they are functions

$$\theta(x) : \mathbb{R}^m \rightarrow \mathbb{R}^n$$

with $m \leq 3N$

Description of a process by collective variables



$$\rho_\theta(z) = \frac{1}{Z} \int dx e^{-\beta U(x)} \delta(\theta(x) - z)$$

$$Z = \int dx e^{-\beta U(x)}$$

$$F(z) = -\frac{1}{\beta} \ln \rho_\theta(z)$$

$$F(z_B) - F(z_A) = \int_{z_A}^{z_B} dz \frac{dF}{dz}$$

$$\frac{dF(z)}{dz} = - \lim_{\beta k \rightarrow \infty} \frac{\int dx k(\theta(x) - z) e^{-\beta U(x)} e^{-\frac{\beta k}{2}(\theta(x) - z)^2}}{\int dx e^{-\beta U(x)} e^{-\frac{\beta k}{2}(\theta(x) - z)^2}}$$

$$U_k(x, z) = U(x) + \frac{k}{2}(\theta(x) - z)^2$$

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Restrained hybrid Monte Carlo

- Random momenta extracted from a Maxwell-Boltzmann distribution at inverse temperature β
- Collective move corresponding to a short MD trajectory with the guiding Hamiltonian $\mathcal{H}_g(x, p) = U(x) + K(p)$
- Acceptance probability is

$$\begin{aligned} P_A(x^{i+1}, p^{i+1} | x^i, p^i) &= \min\{1, e^{-\beta \delta \mathcal{H}_a}\} \\ \delta \mathcal{H}_a &= \mathcal{H}_a(x^{i+1}, p^{i+1}) - \mathcal{H}_a(x^i, p^i) \\ \mathcal{H}_a(x, p) &= U_k(x, z) + K(p) \end{aligned}$$

- δt determines the acceptance rate
- $\mathcal{H}_a(x, p) \neq \mathcal{H}_g(x, p)$

S. Duane, *Phys. Lett. B*, 1987, **195**, p. 216

B. Mehlig, D. W. Heermann & B. Forrest, *Phys. Rev. B*, 1992, **45**, p. 679

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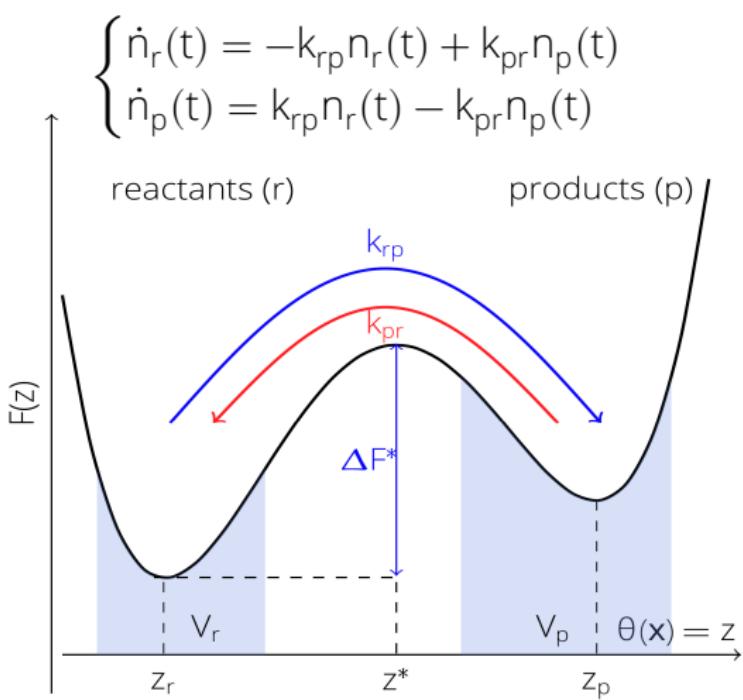
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Rate constant calculation



$$N_r + N_p \approx 1$$

$$N_r = \frac{1}{Z} \int_{V_r} dx e^{-\beta U(x)}$$

$$N_p = \frac{1}{Z} \int_{V_p} dx e^{-\beta U(x)}$$

$$k_{rp} = \frac{v}{2N_r}$$

$$k_{pr} = \frac{v}{2N_p}$$

$$v = \lim_{\tau \rightarrow \infty} \frac{N_\tau^{rp}}{\tau}$$

TST with dynamical corrections

$$\nu = \int d\mathbf{x} dv \dot{\theta}(\mathbf{x}) \xi_p(\mathbf{x}, v) \xi_r(\mathbf{x}, -v) \rho(\mathbf{x}, v) \delta(\theta(\mathbf{x}) - z^*)$$

$$= \frac{\int d\mathbf{x} dv \dot{\theta}(\mathbf{x}) \xi_p(\mathbf{x}, v) \xi_r(\mathbf{x}, -v) \rho(\mathbf{x}, v) \delta(\theta(\mathbf{x}) - z^*)}{\int d\mathbf{x} dv \rho(\mathbf{x}, v) \delta(\theta(\mathbf{x}) - z^*)} \int d\mathbf{x} dv \rho(\mathbf{x}, v) \delta(\theta(\mathbf{x}) - z^*)$$

$$= \langle \dot{\theta}(\mathbf{x}) \xi_p(\mathbf{x}, v) \xi_r(\mathbf{x}, -v) \rangle_z e^{-\beta F(z^*)}$$

- $\xi_p(\mathbf{x}, v)$ is the probability to reach p before z^* starting from (\mathbf{x}, v)
- $\xi_r(\mathbf{x}, -v)$ is the probability to reach r before p starting from $(\mathbf{x}, -v)$

$$\nu = \frac{e^{-\beta F(z^*)}}{N_s} \sum_{i=1}^{N_s} \dot{\theta}(\mathbf{x}_i) \chi_p^i \chi_r^i$$

$$\dot{\theta}(\mathbf{x}_i(t=0)) = \frac{\theta(\mathbf{x}_i(\delta t)) - \theta(\mathbf{x}_i(-\delta t))}{2\delta t}$$

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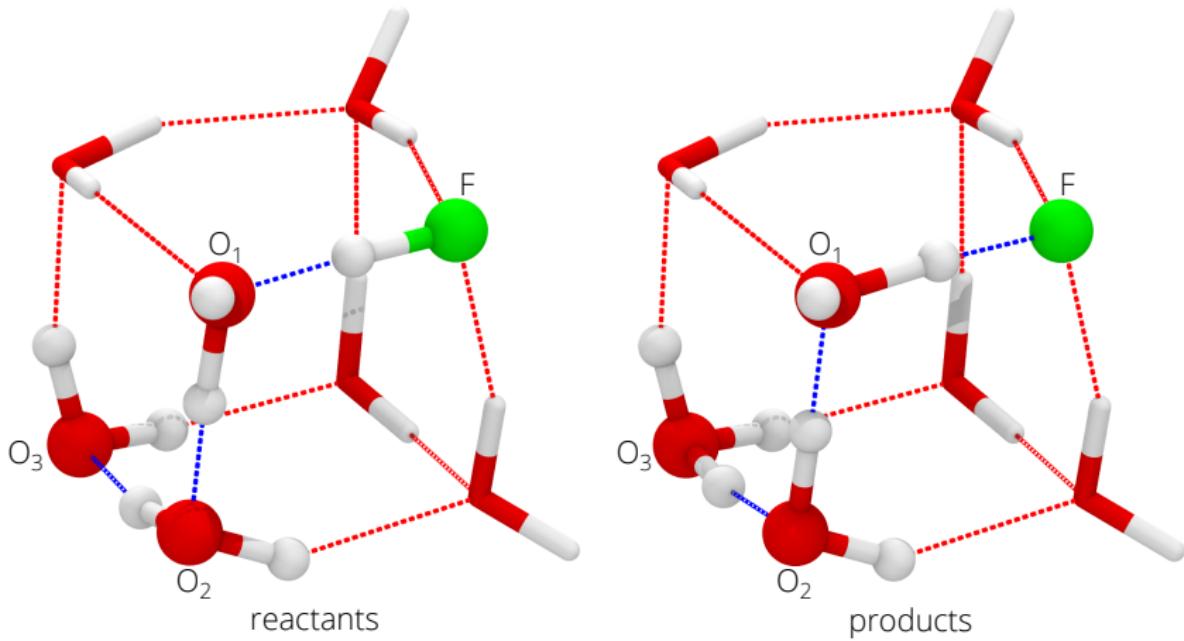
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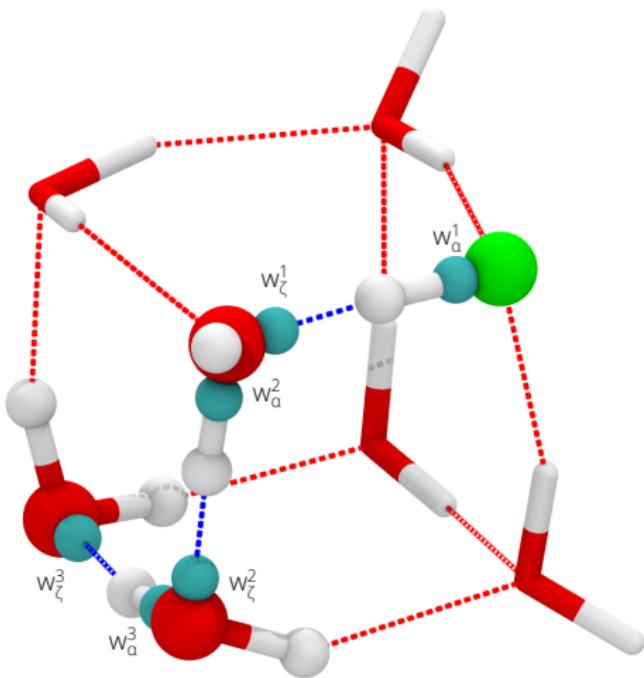
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Collective variable for acid dissociation



Collective variable for acid dissociation



$$\langle \mathcal{H}_{KS} \rangle_a = \langle w_a | \mathcal{H}_{KS}(x) | w_a \rangle$$

$$\langle \mathcal{H}_{KS} \rangle_\zeta = \langle w_\zeta | \mathcal{H}_{KS}(x) | w_\zeta \rangle$$

$$w_\chi(r) = \sum_i c_{\chi,ii}(r)$$

$$\xi_i(x) = \langle \mathcal{H}_{KS} \rangle_\zeta - \langle \mathcal{H}_{KS} \rangle_a$$

$\xi_i < 0$ covalent bond at a

$\xi_i > 0$ covalent bond at ζ

$$\theta(x) = \sum_{i=1}^3 \xi_i(x)$$

G. Berghold, C. Mundy, A. Romero, J. Hutter & M. Parrinello, *Phys. Rev. B*, 2000, **61**, p. 10040

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Computational details

- Restrained hybrid Monte Carlo developed and implemented in CP2K
- DFT-GPW, HCTH120 exchange correlation functional, GTH pseudo-potentials, m-TZV2P basis set, cubic box of side 14.0 Å and a plane wave cut-off of 300 Ry
- 24k hMC steps per z point to converge the mean force (relative error $\approx 10^{-4}$)
- Almost uniform grid in z space, [-16.6,16.3] eV, with an average step of 0.95 eV
- $k = 50 \text{ eV}^{-1}$ for the biased potential
- $T = 25, 75, 150, 225$ and 300 K

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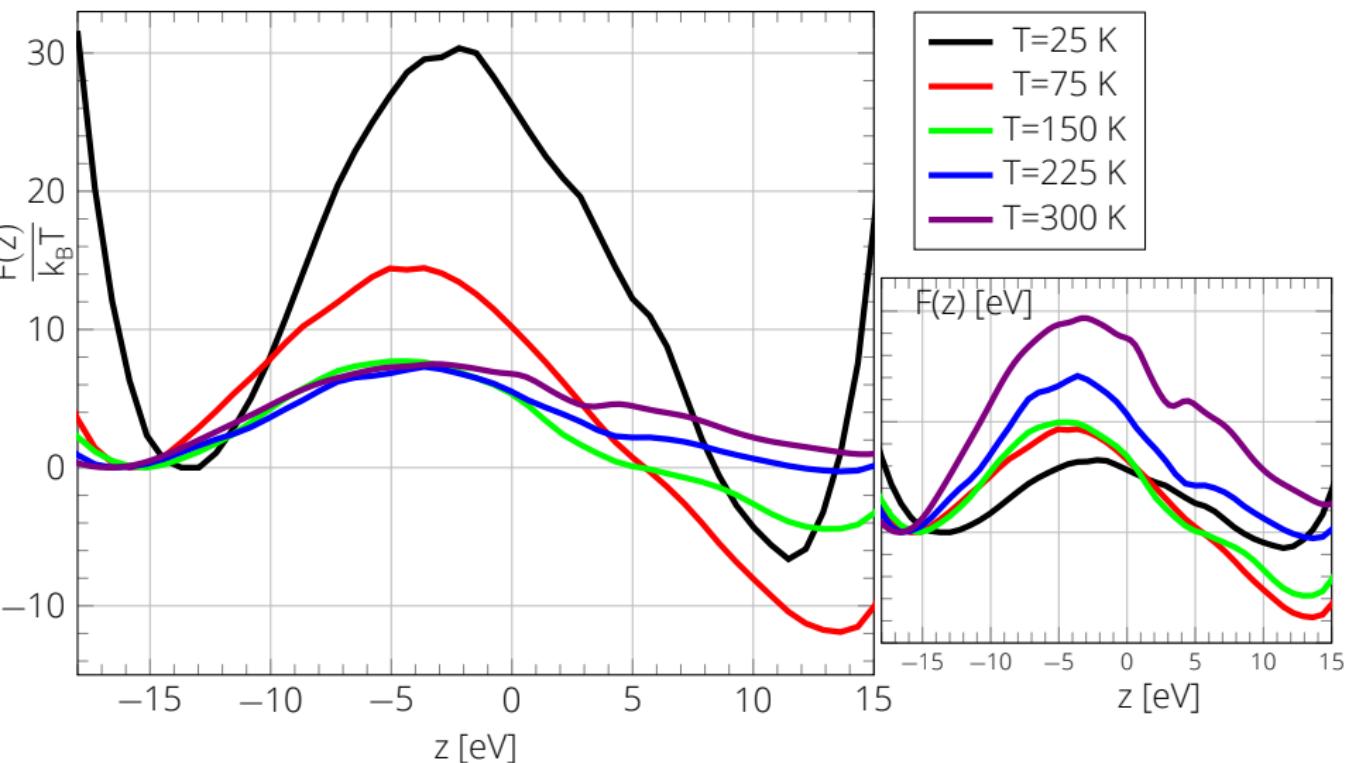
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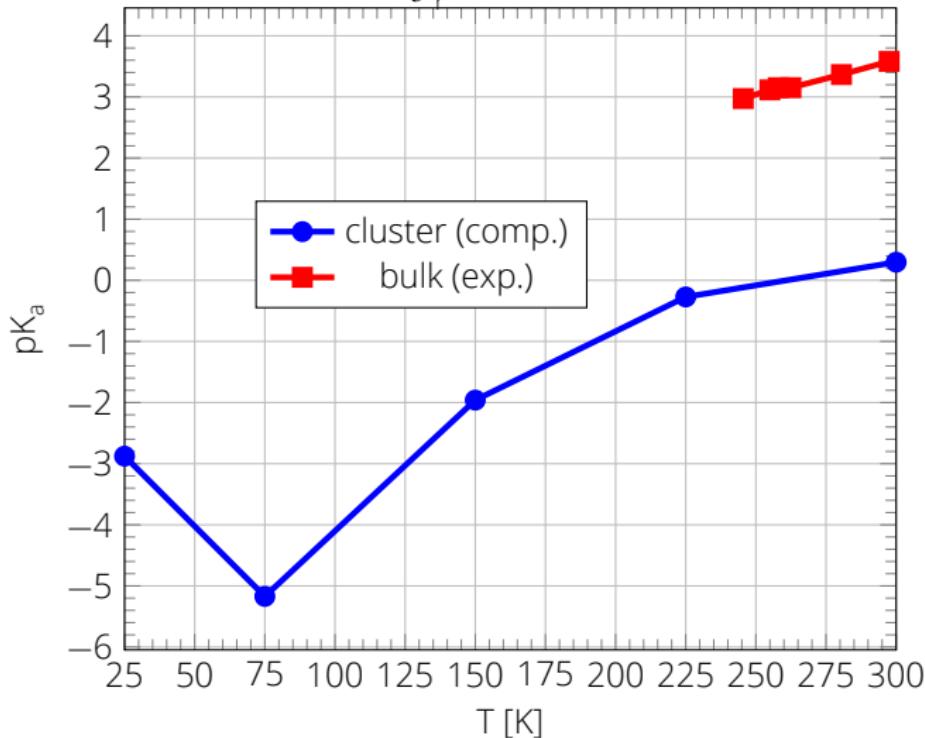
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Free energy profile

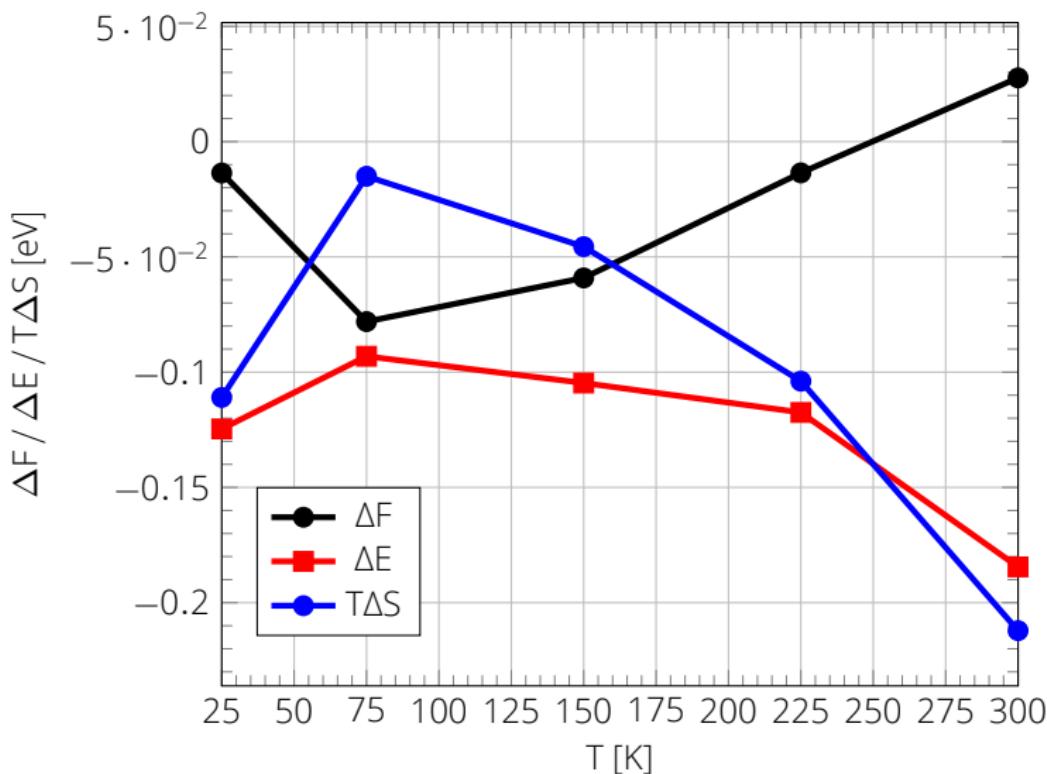


pK_a

$$K_a = \frac{\mathcal{P}_p}{\mathcal{P}_r} \quad pK_a = -\log K_a$$

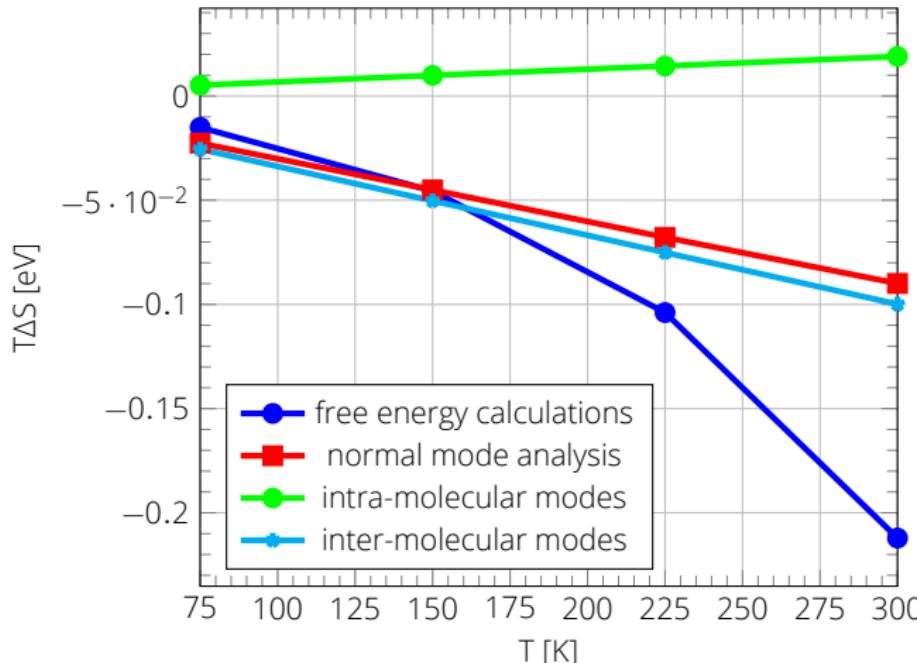


Contributions to the free energy



Entropy

$$S_{\text{h-vib}} = \sum_{i=1}^{N_m} \left\{ \frac{\beta h v_i e^{-\frac{\beta h v_i}{2}}}{1 - e^{-\frac{\beta h v_i}{2}}} - \ln \left(1 - e^{-\frac{\beta h v_i}{2}} \right) \right\}$$



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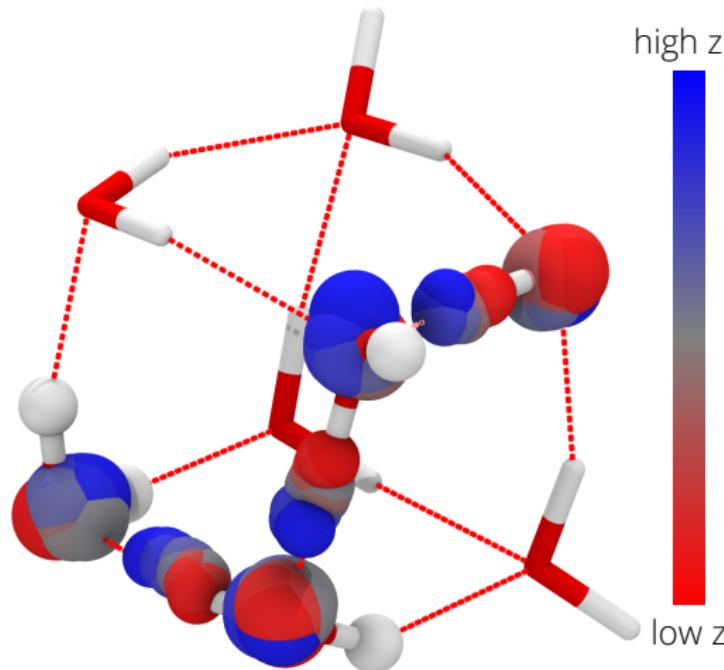
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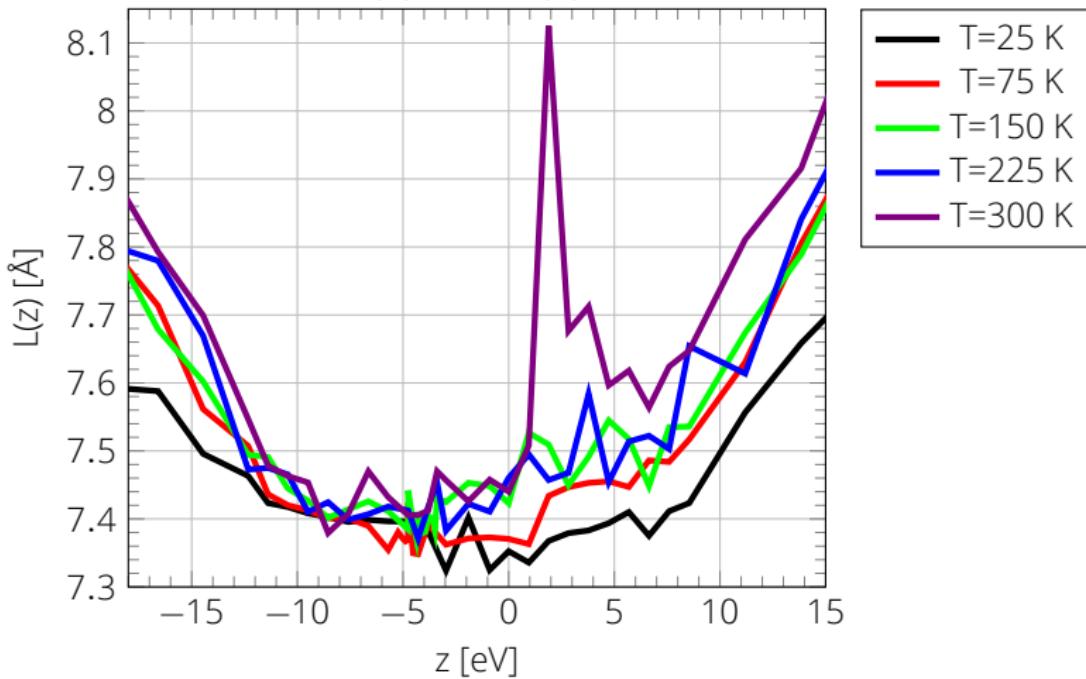
Mean path

$$\mathbf{x}(z) = \langle \mathbf{x} \rangle_z$$



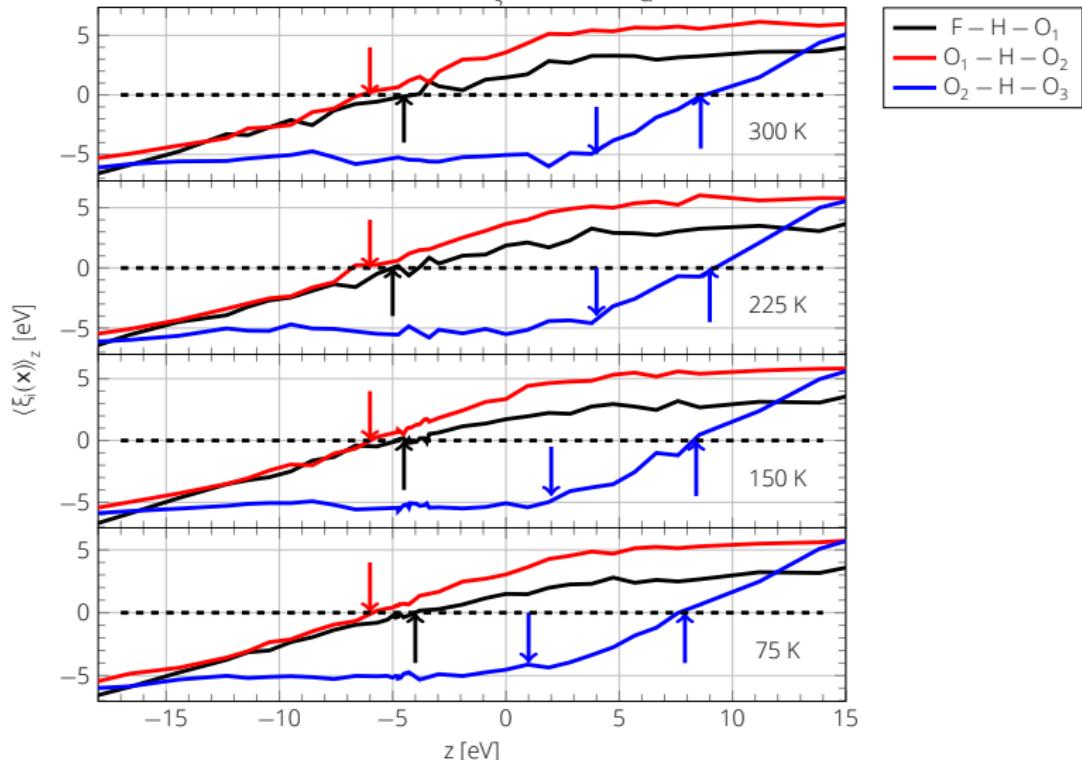
Hydrogen bond chain length

$$L(z) = \sum_{i=1}^3 d_i(z) = \sum_{i=1}^3 \|r_i^a(z) - r_i^\zeta(z)\|_2^{1/2}$$

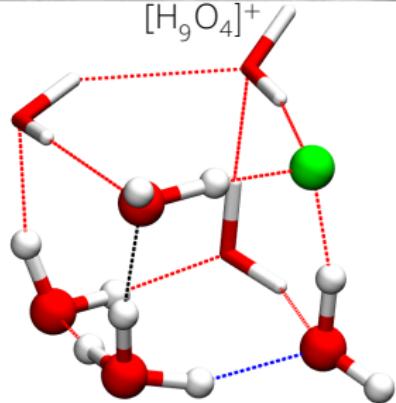
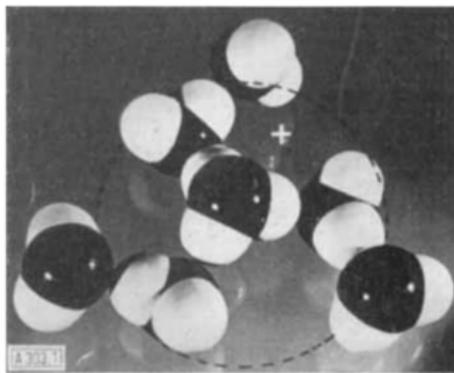


ξ_i VS Z

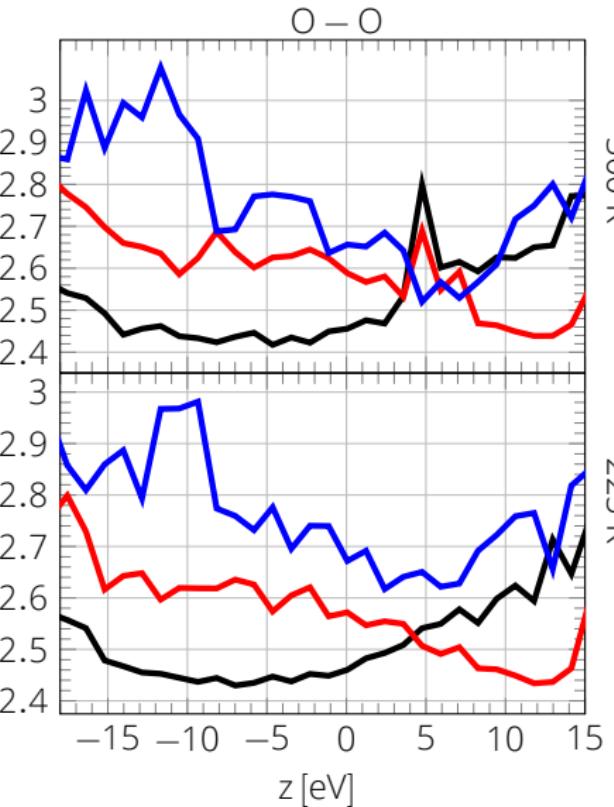
$$\xi_i(x) = \langle \mathcal{H}_{KS} \rangle_z - \langle \mathcal{H}_{KS} \rangle_a$$



Intermediate state



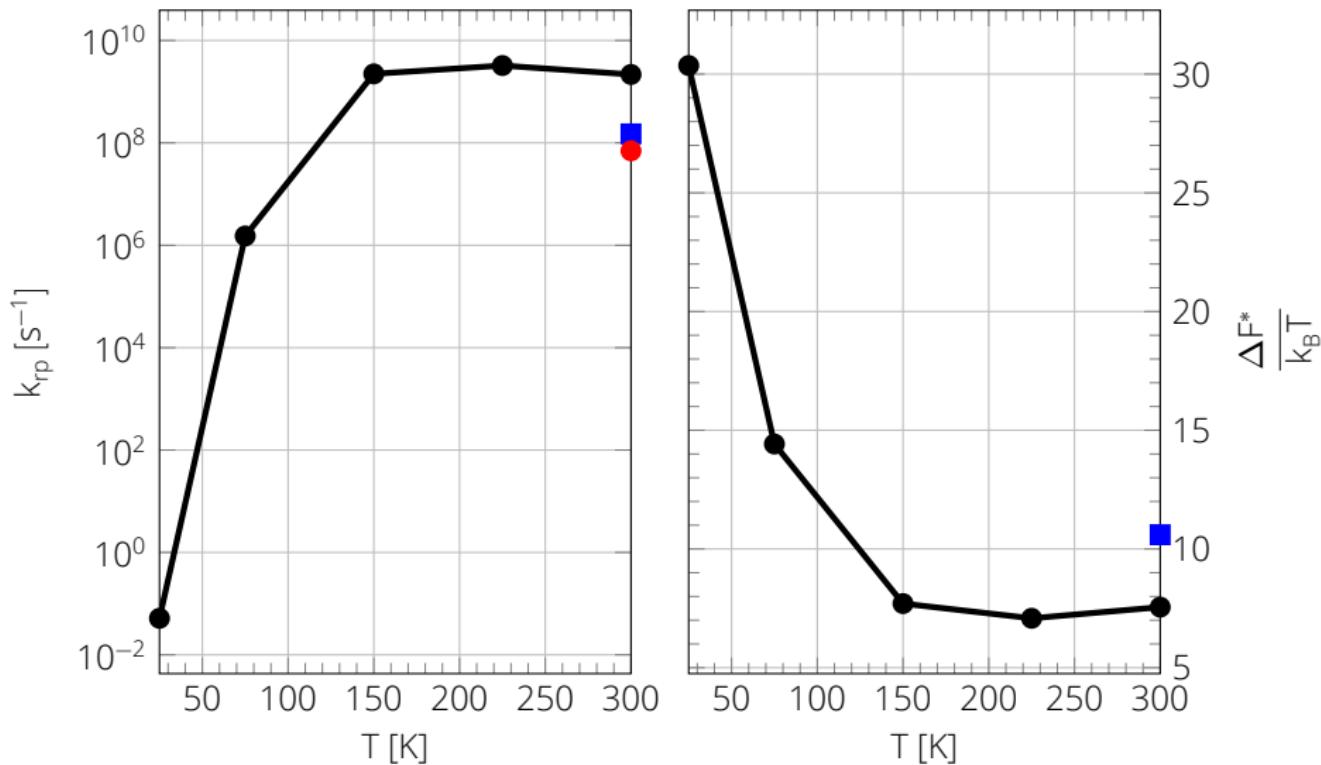
M. Eigen, *Angew. Chem. Int. Ed. Engl.* 1964, 3, p. 1



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Reaction rate constant



T. Joutsuka & K. Ando, *J. Chem. Phys.*, 2011, 115, p. 671

M. Eigen, W. Kruse, G. Maass & L. de Maeyer, *Progress in Reaction Kinetics*, 1964, vol. II, p. 285

Summary

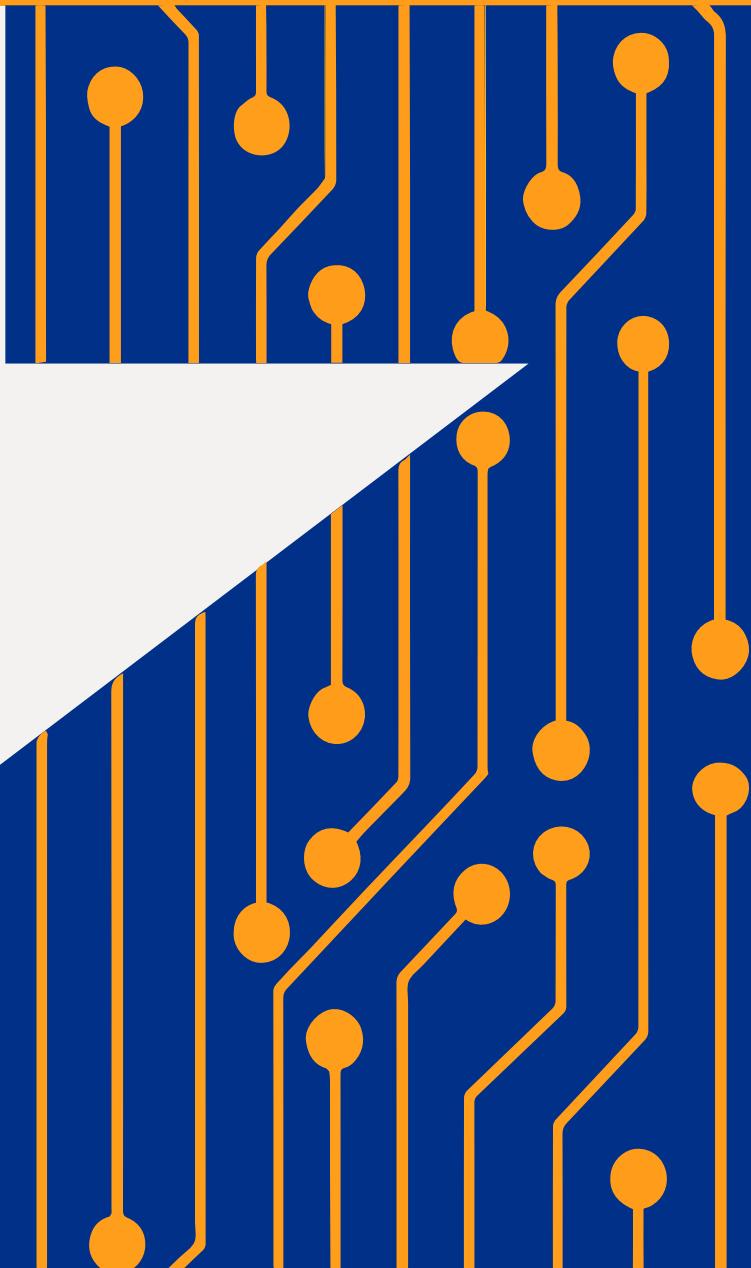
- We studied dissociation reaction of HF in water clusters by using statistical mechanics of rare events combined with *ab initio* MD
- RhMC was implemented in CP2K
- We developed a CV which is able to monitor and steer the reaction without any strong *a priori* knowledge of the mechanism
- HF is a stronger acid in cluster than in bulk
- HF gets a strong acid at lower T

Summary

- Weak acidity of HF has an entropic origin
- Negative ΔS is due to two opposite contributions a positive intra-molecular one and a dominant negative inter-molecular
- The deprotonation process is "cooperative" but asynchronous and triggered by the compression of HB chain
- Reaction rate constant in cluster is higher than in bulk



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Questions?





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Thank you

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