HF Dissociation in Water Clusters by Computer Simulations*

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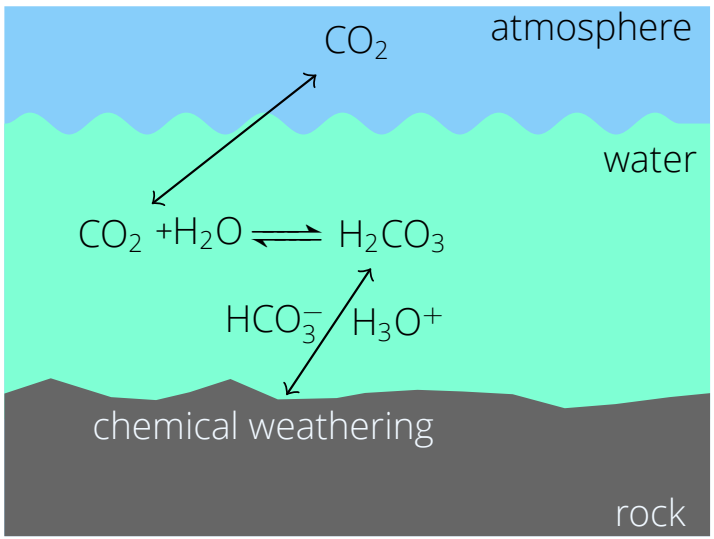
Outline

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

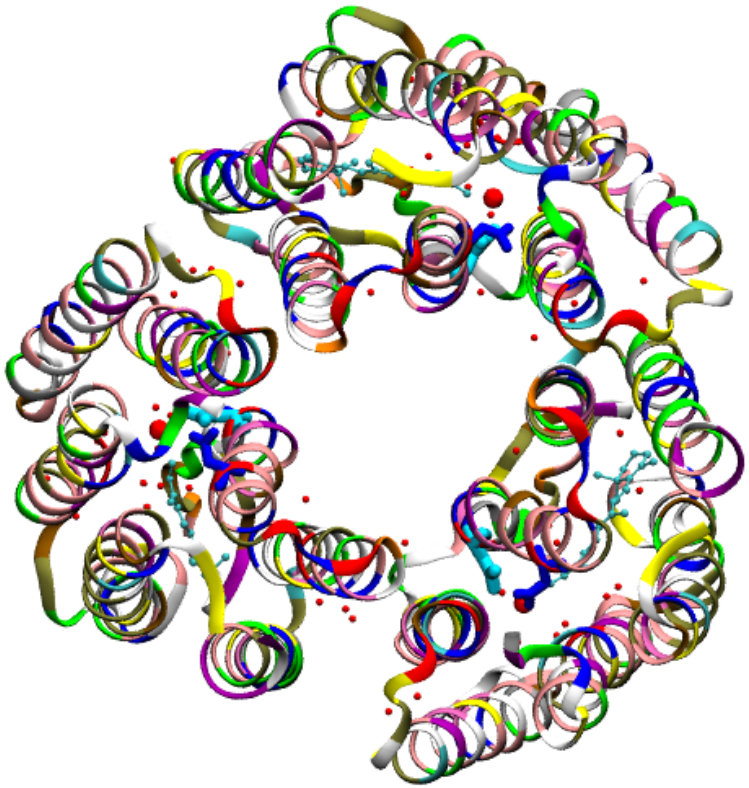
Acid dissociation

$$(AH)_{aq} \rightleftharpoons (A^-)_{aq} + (H^+)_{aq}$$

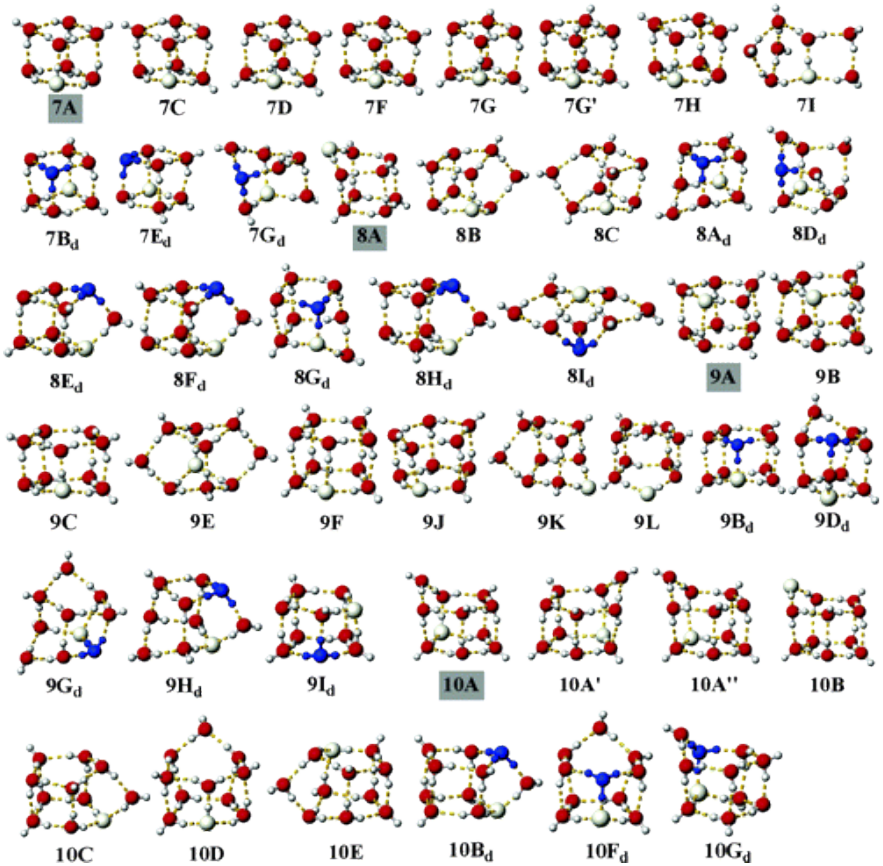
carbon cycle



biological systems



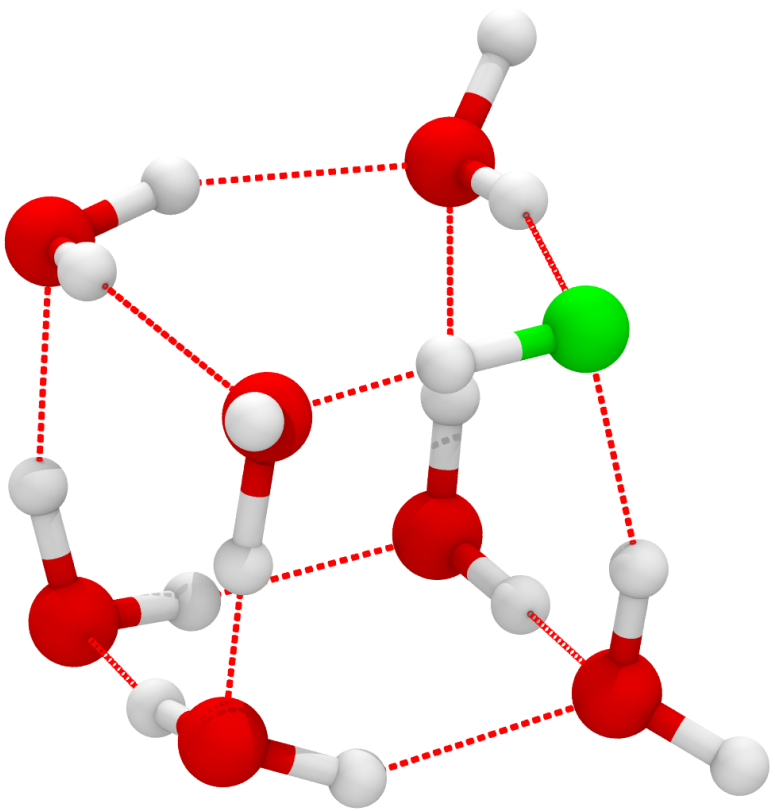
HF dissociation



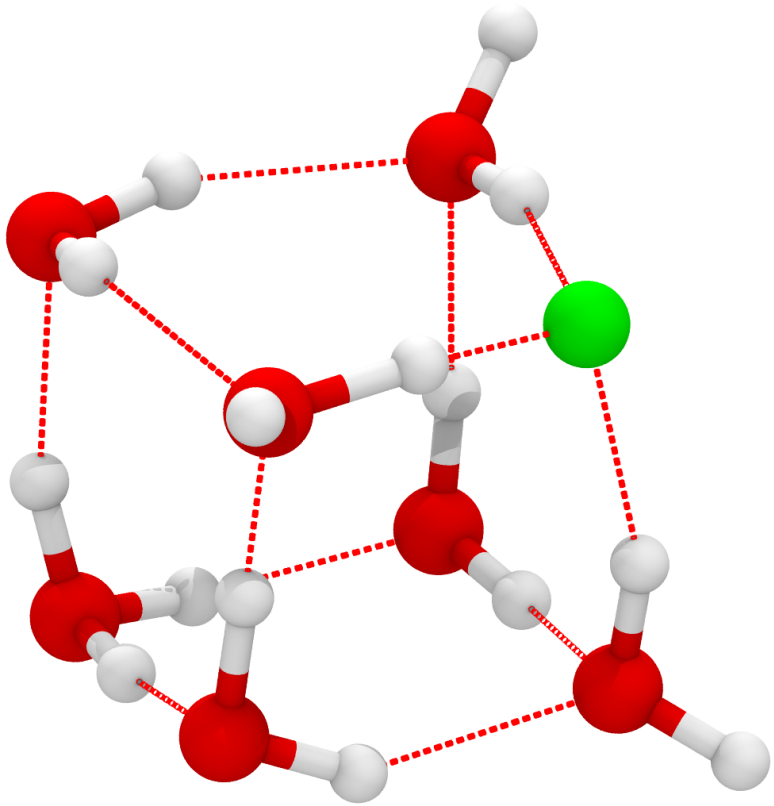
- Atmospheric chemistry, pockets in proteins...
- Testing ground for development of models for dissociaiton reaction in bulk

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 $HF(H_2O)_7$



reactants



products

J.-L. Kuo & M. L. Klein, *J. Chem. Phys.* 2004, **120**, p. 4690

Objectives

- Equilibrium constant
- Reaction mechanism
- Reaction rate constant

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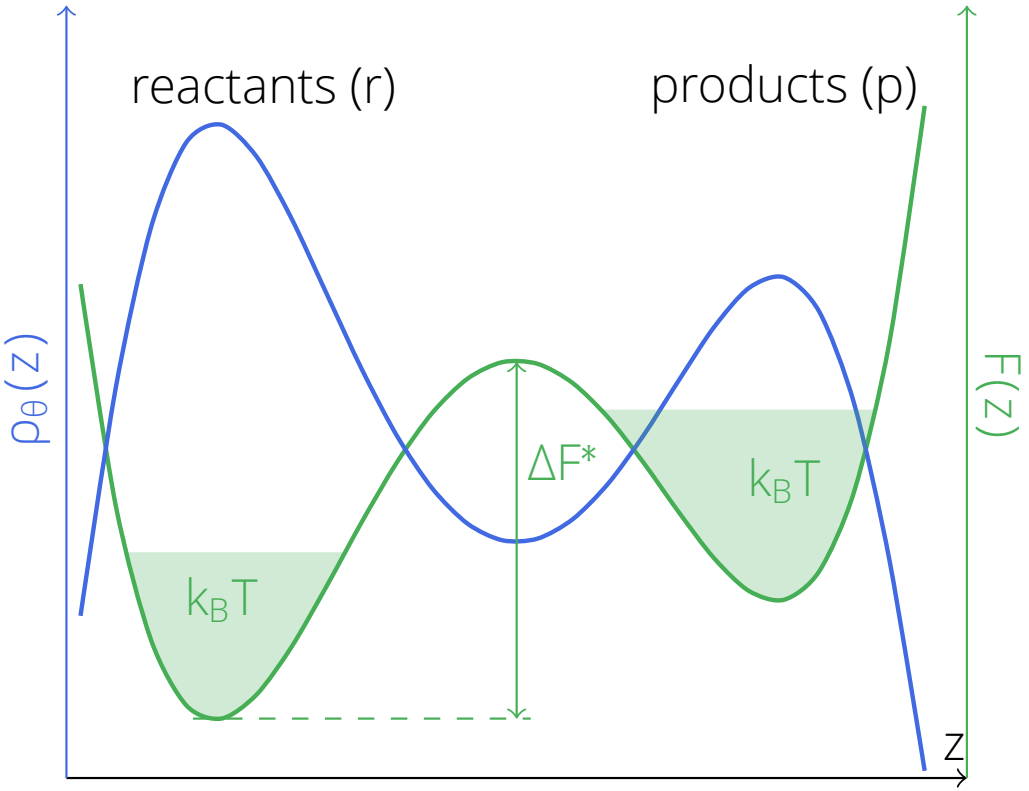
Description of a process by collective variables



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

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

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

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

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

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

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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 $\mathcal{H}_g(\mathbf{x},\mathbf{p}) = U(\mathbf{x}) + K(\mathbf{p})$
- Acceptance probability is

$$P_A(\mathbf{x}^{i+1},\mathbf{p}^{i+1}|\mathbf{x}^i,\mathbf{p}^i) = \min\left\{1, e^{-\beta\delta\mathcal{H}_a}\right\}$$
$$\delta\mathcal{H}_a = \mathcal{H}_a(\mathbf{x}^{i+1},\mathbf{p}^{i+1}) - \mathcal{H}_a(\mathbf{x}^i,\mathbf{p}^i)$$
$$\mathcal{H}_a(\mathbf{x},\mathbf{p}) = U_k(\mathbf{x},z) + K(\mathbf{p})$$

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

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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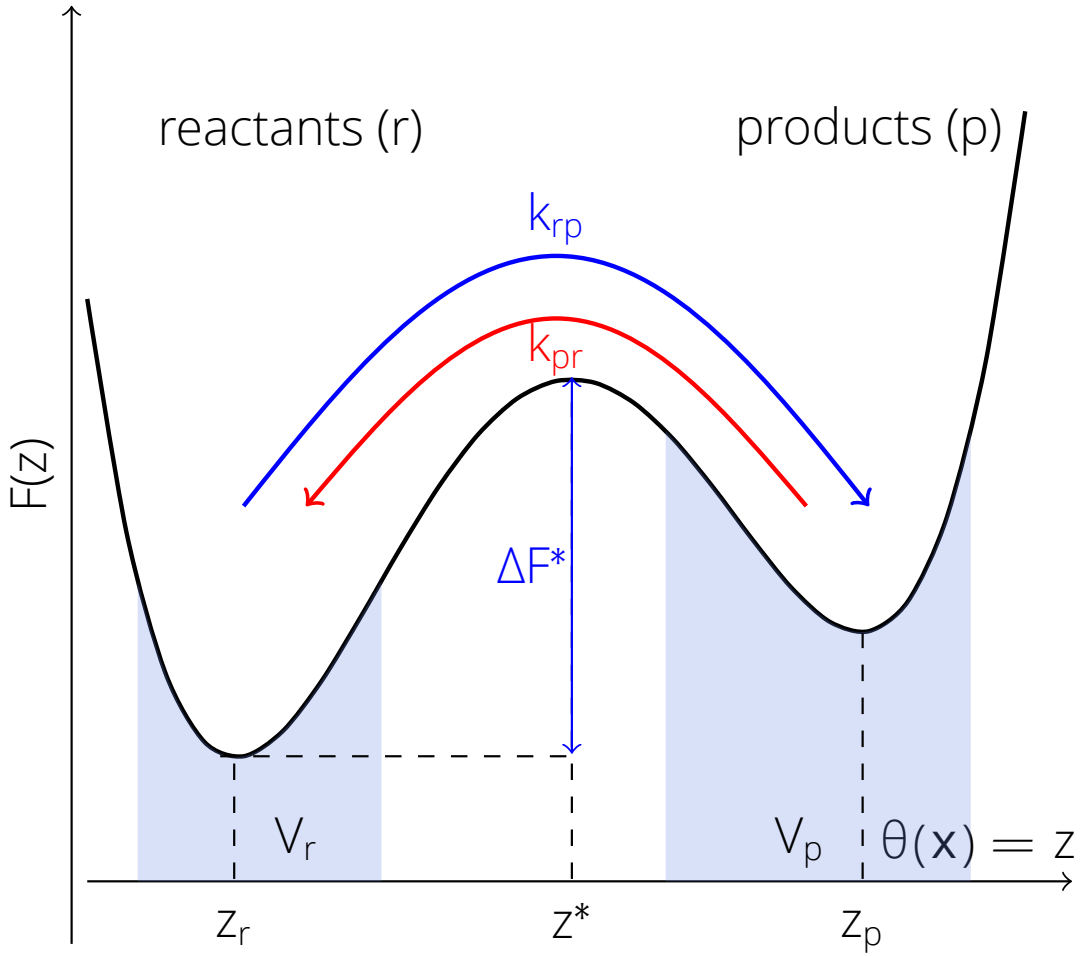
Rate constant calculation

$$\begin{cases} \dot{n}_r(t) = -k_{rp} n_r(t) + k_{pr} n_p(t) \\ \dot{n}_p(t) = k_{rp} n_r(t) - k_{pr} n_p(t) \end{cases}$$



E. Vanden-Eijnden & F. A. Tal, *J. Chem. Phys.* 2005, **123**, p. 184103

$$N_r + N_p \approx 1$$

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

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

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

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

$$\nu = \lim_{\tau \to \infty} \frac{N_\tau^{rp}}{\tau}$$

TST with dynamical corrections

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

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

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

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

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

$$\dot{\theta}(x_i(t=0)) = \frac{\theta\big(x_i(\delta t)\big)-\theta\big(x_i(-\delta t)\big)}{2\delta t}$$

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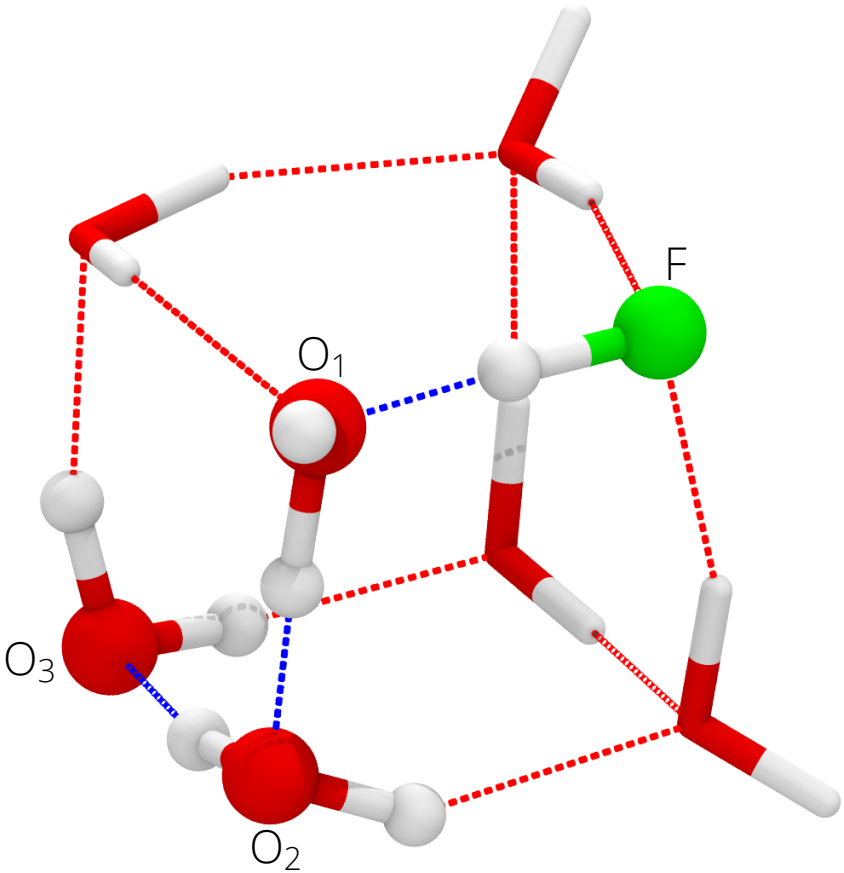
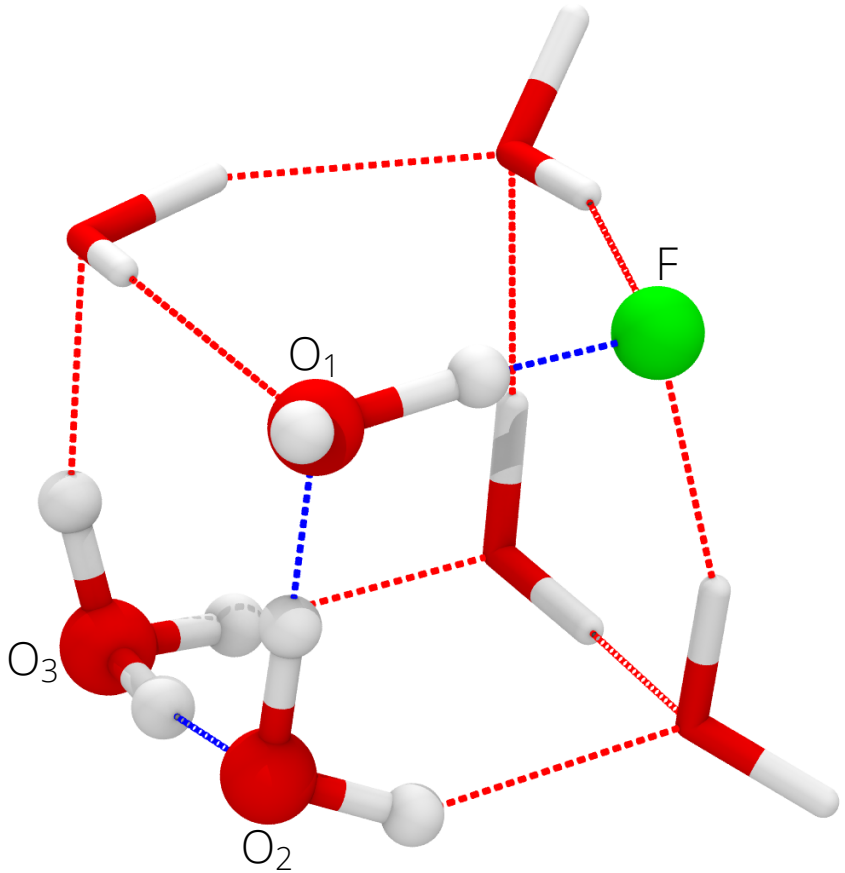
Collective variable for acid dissociation

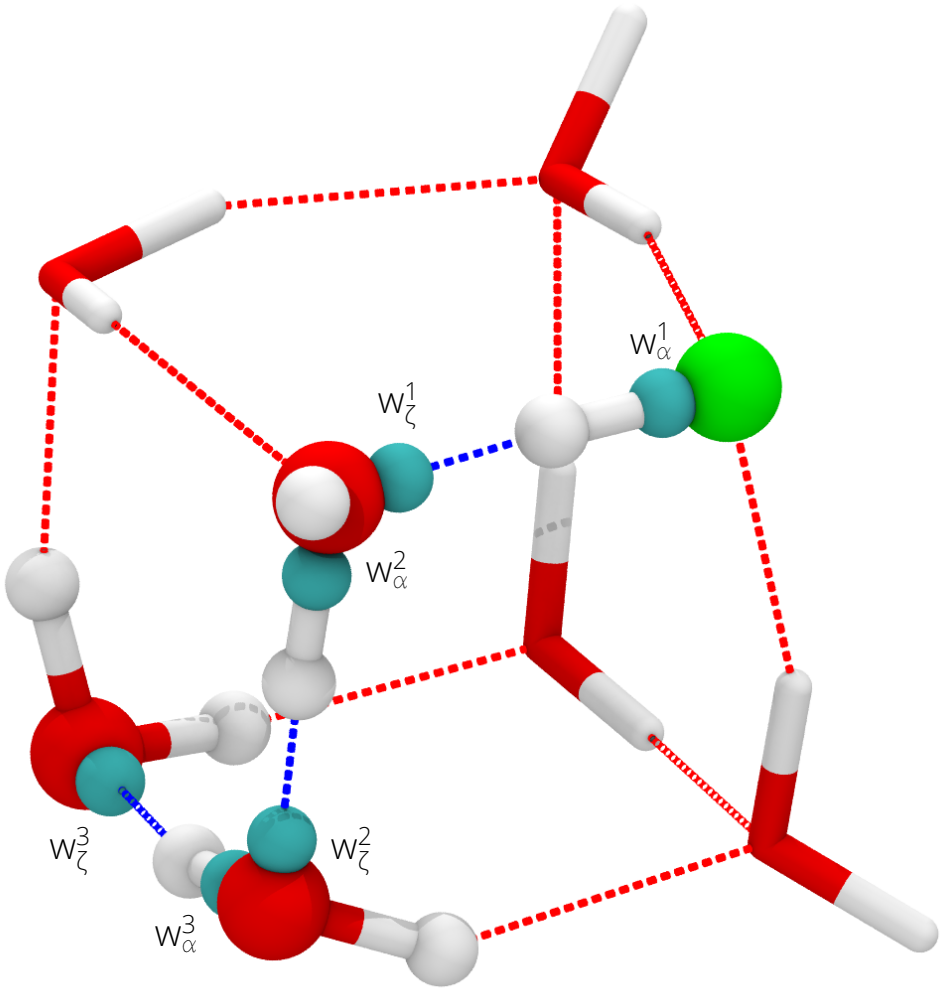


reactants



products

Collective variable for acid dissociation



$$\langle \mathcal{H}_{KS} \rangle_\alpha = \langle w_\alpha \mid \mathcal{H}_{KS}(\mathbf{x}) \mid w_\alpha \rangle$$
$$\langle \mathcal{H}_{KS} \rangle_\zeta = \langle w_\zeta \mid \mathcal{H}_{KS}(\mathbf{x}) \mid w_\zeta \rangle$$
$$w_\chi(\mathbf{r}) = \sum_i c_{\chi,i}\phi_i(\mathbf{r})$$

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

$\xi_i < 0$ covalent bond at α

$\xi_i > 0$ covalent bond at ζ

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

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
- $k = 50$ eV^{-1} for the biased potential
- $T = 25$, 75, 150, 225 and 300 K

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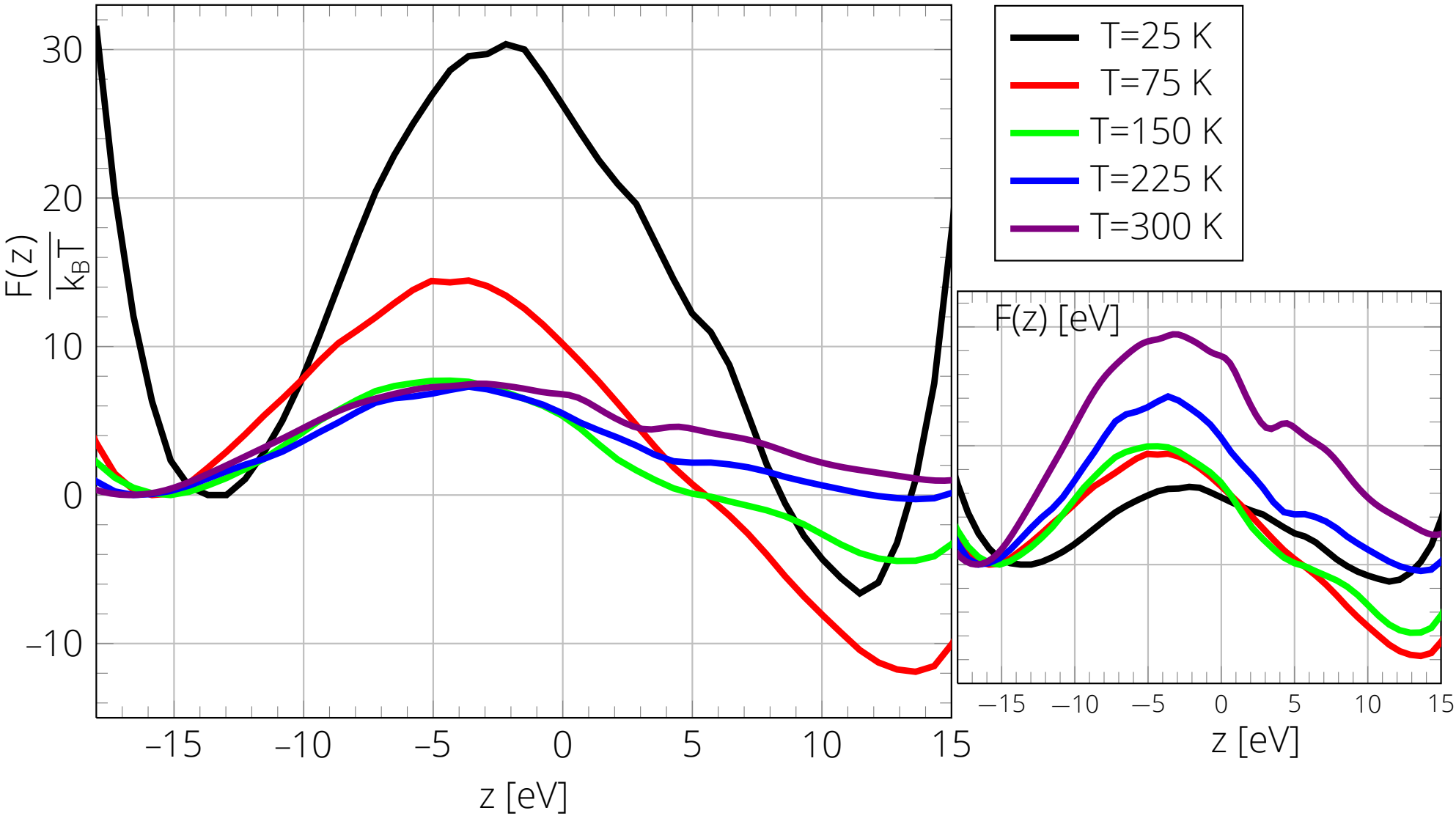
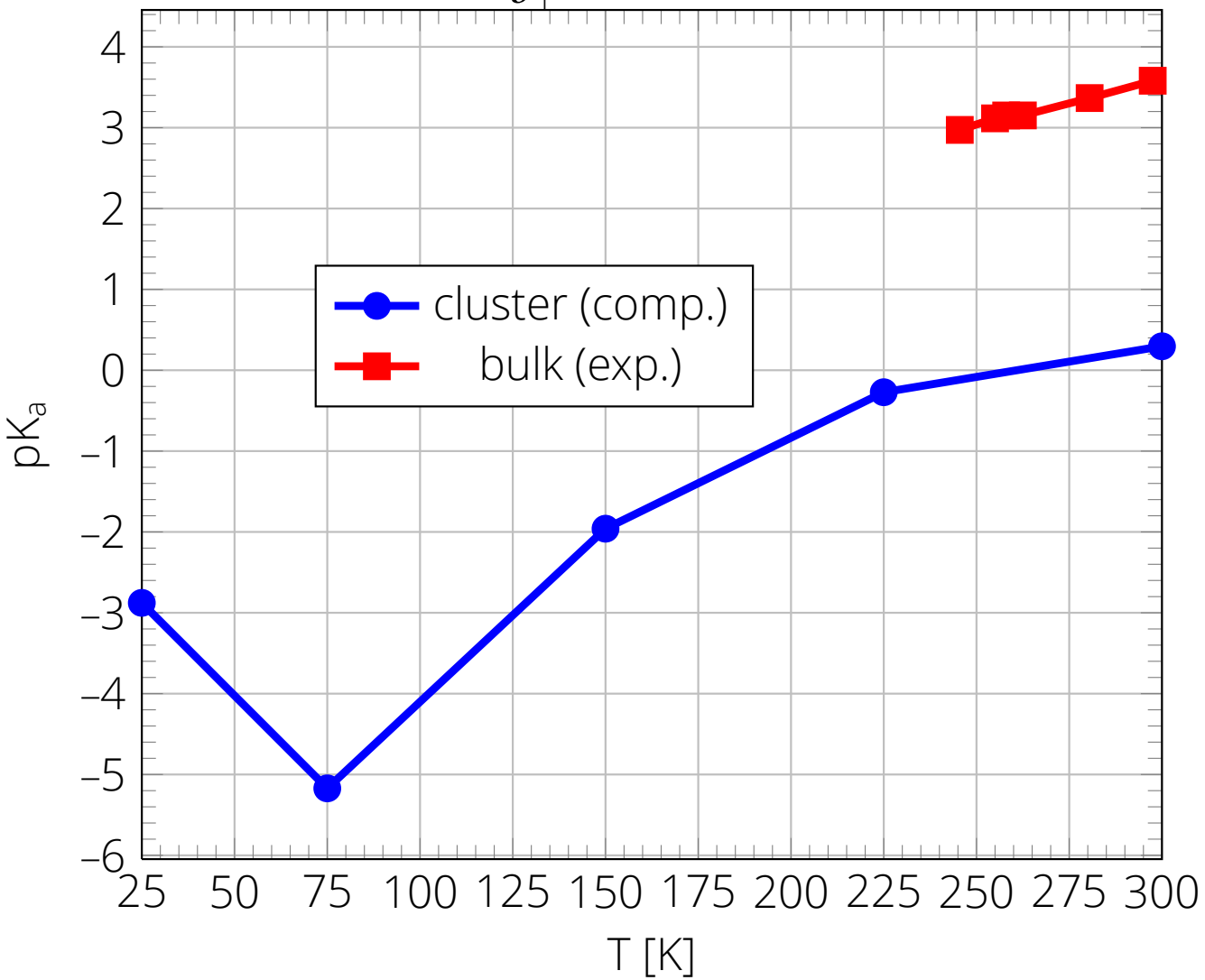
Free energy profile

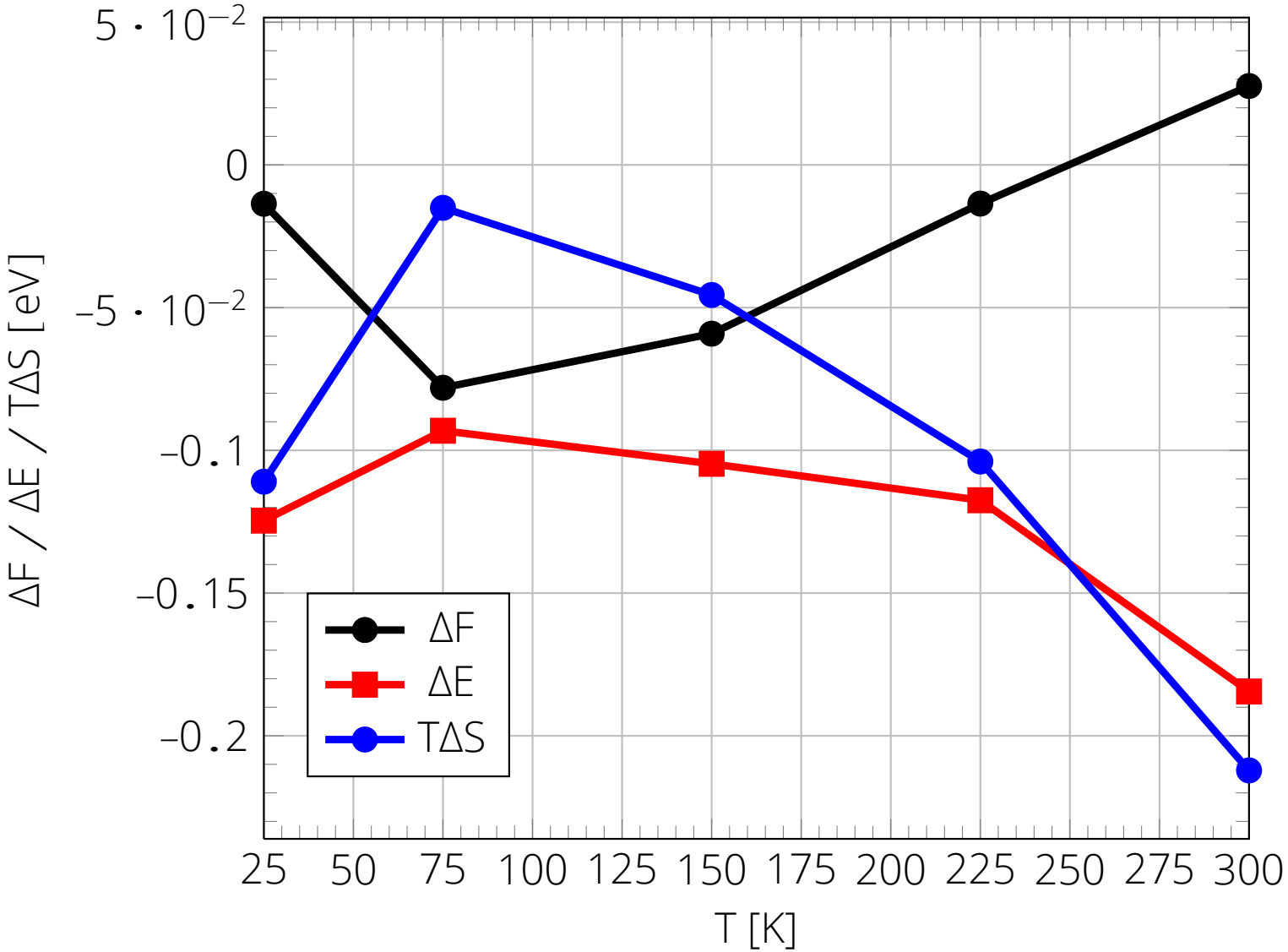


pK_a

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

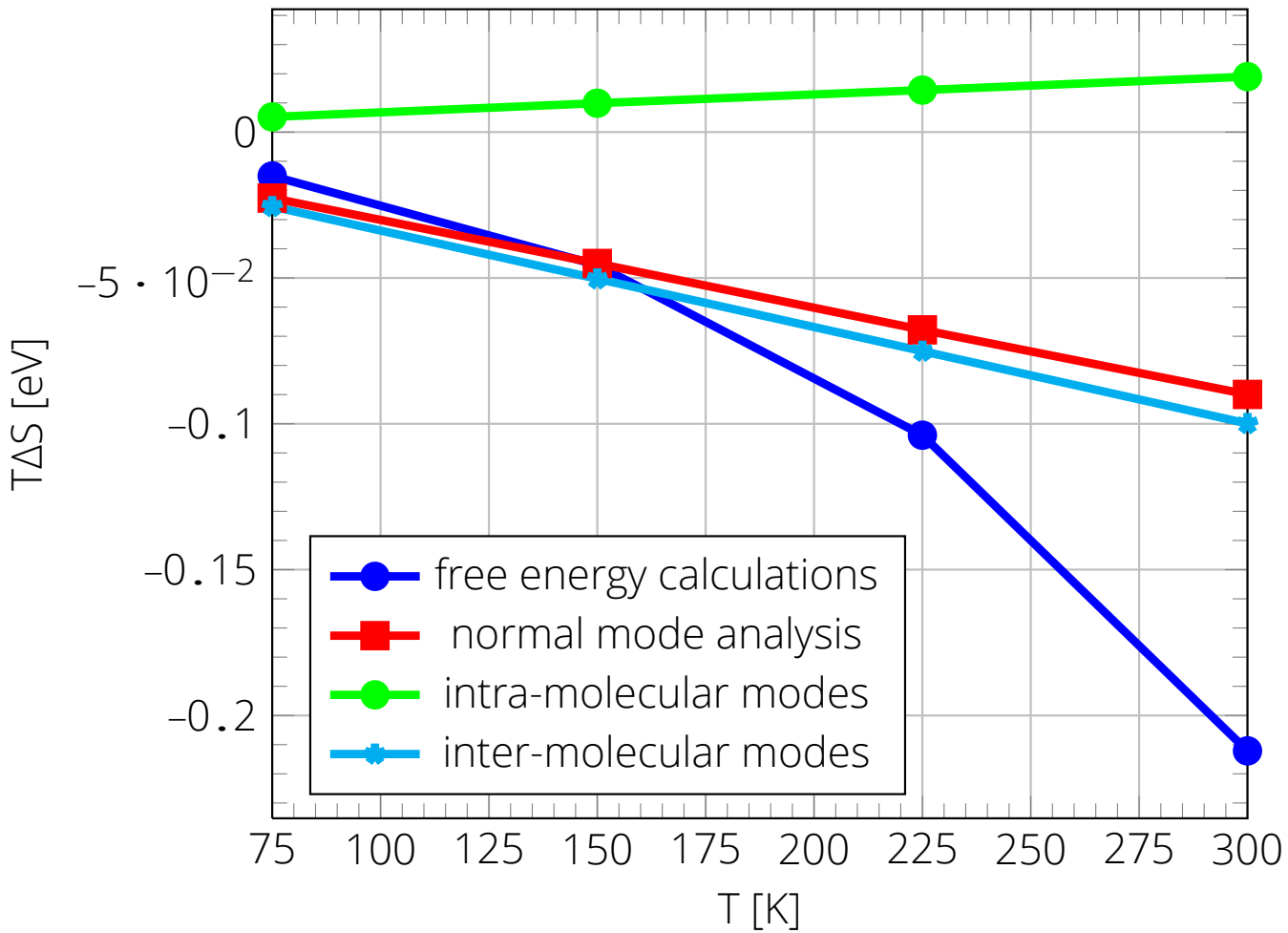


Contributions to the free energy



Entropy

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



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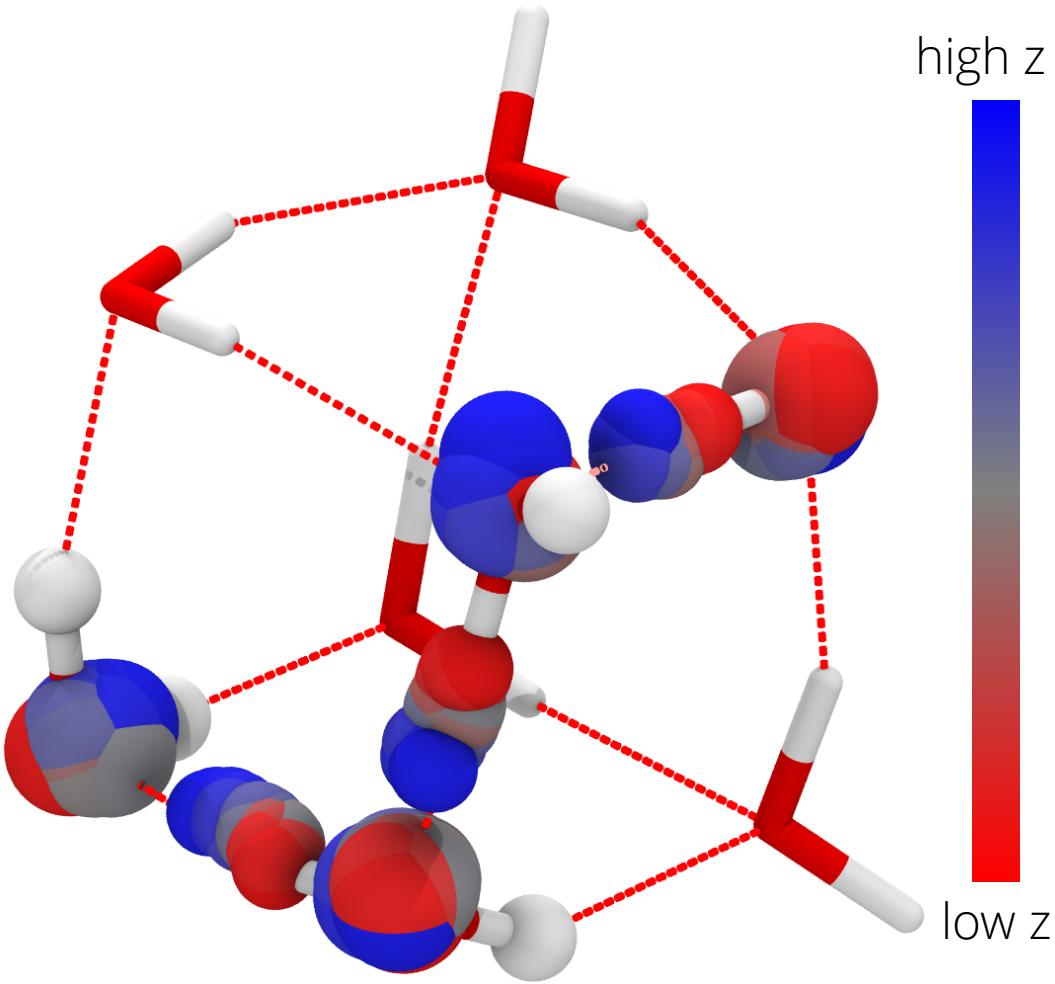
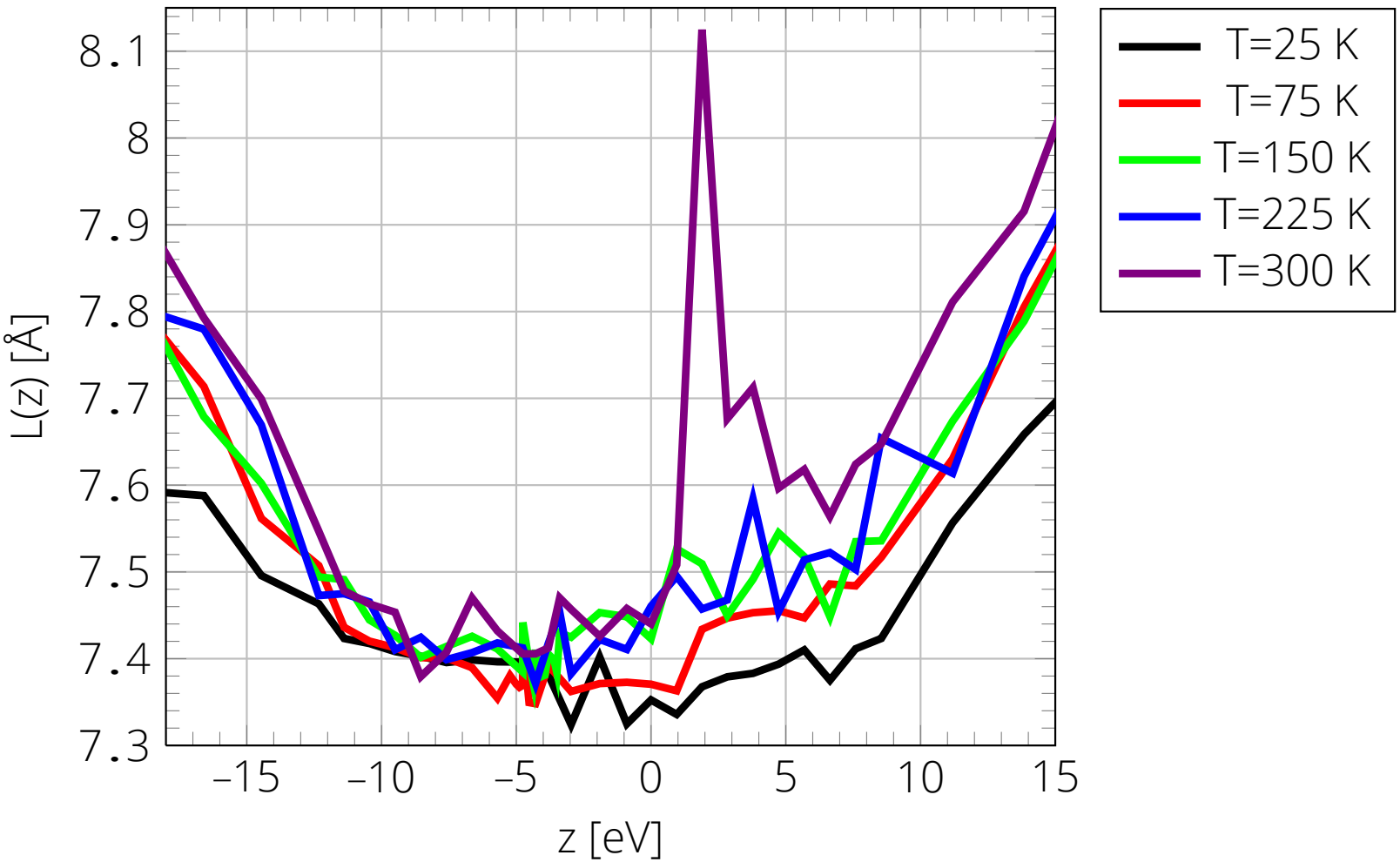
Mean path

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

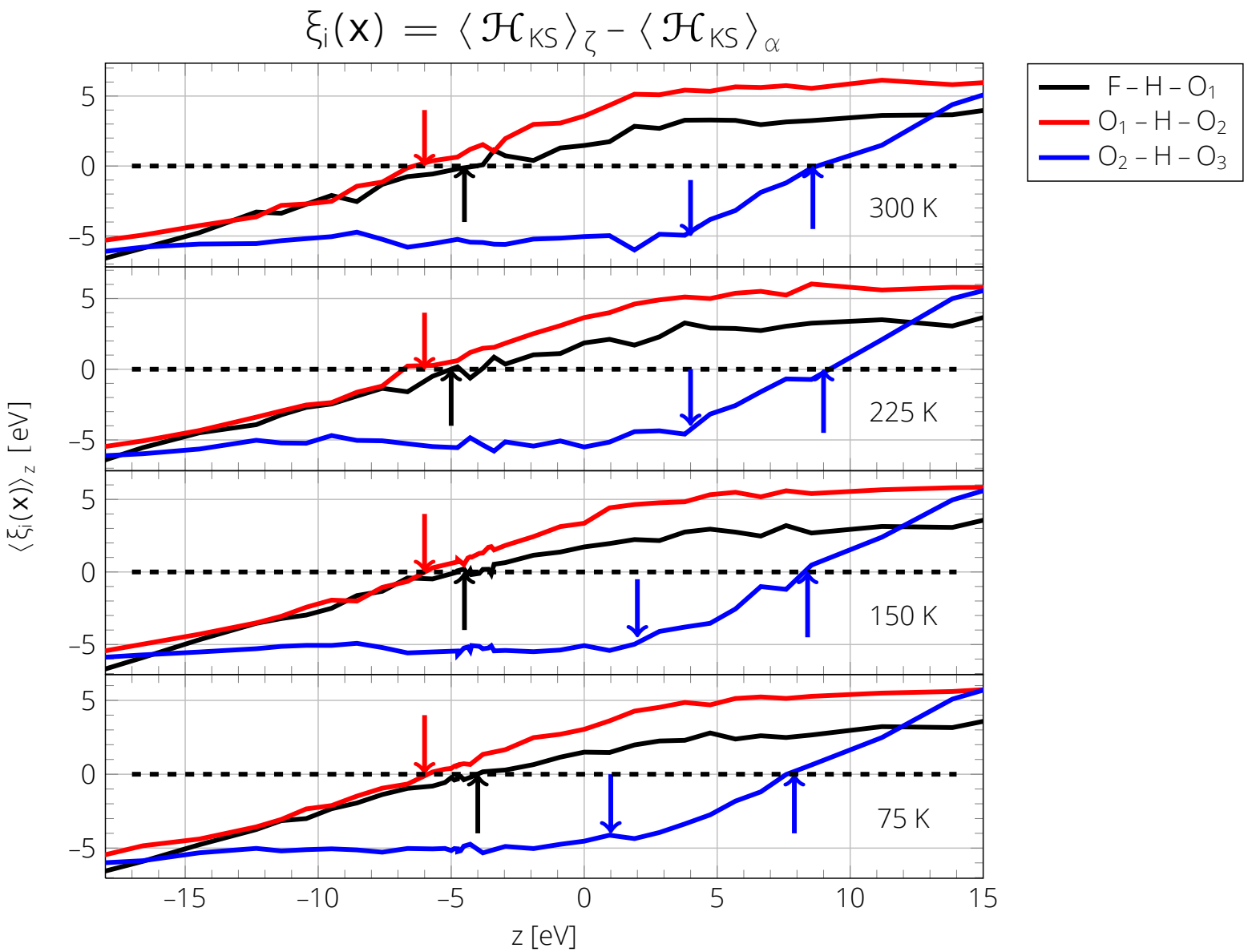


Hydrogen bond chain length

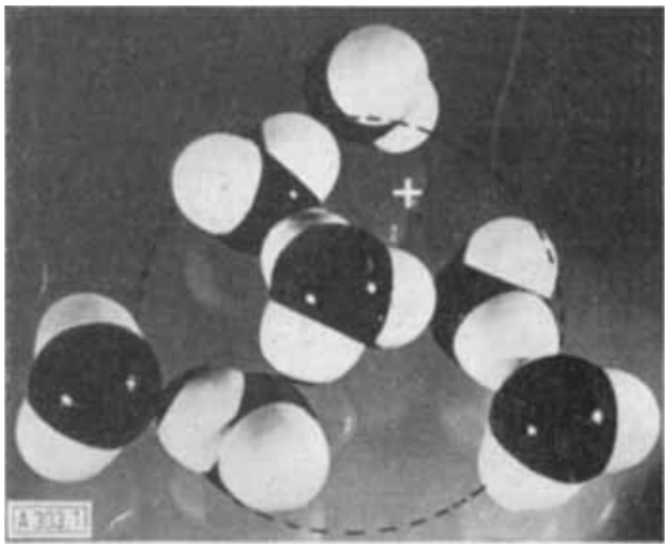
$$L(z) = \sum_{i=1}^{3} d_i(z) = \sum_{i=1}^{3} \| r_i^{\alpha}(z) - r_i^{\zeta}(z) \|_2^{1/2}$$



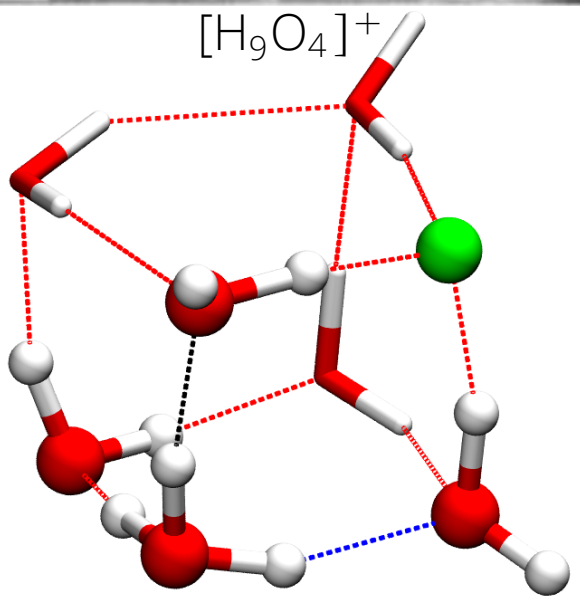
ξ_i *vs z*


$\xi_i(x) = \langle \mathcal{H}_{KS} \rangle_\zeta - \langle \mathcal{H}_{KS} \rangle_\alpha$
F – H – O1
O1 – H – O2
O2 – H – O3
300 K
225 K
150 K
75 K
5
0
−5
−15
−10
−5
0
5
10
15
z [eV]
⟨ξi(x)⟩z [eV]

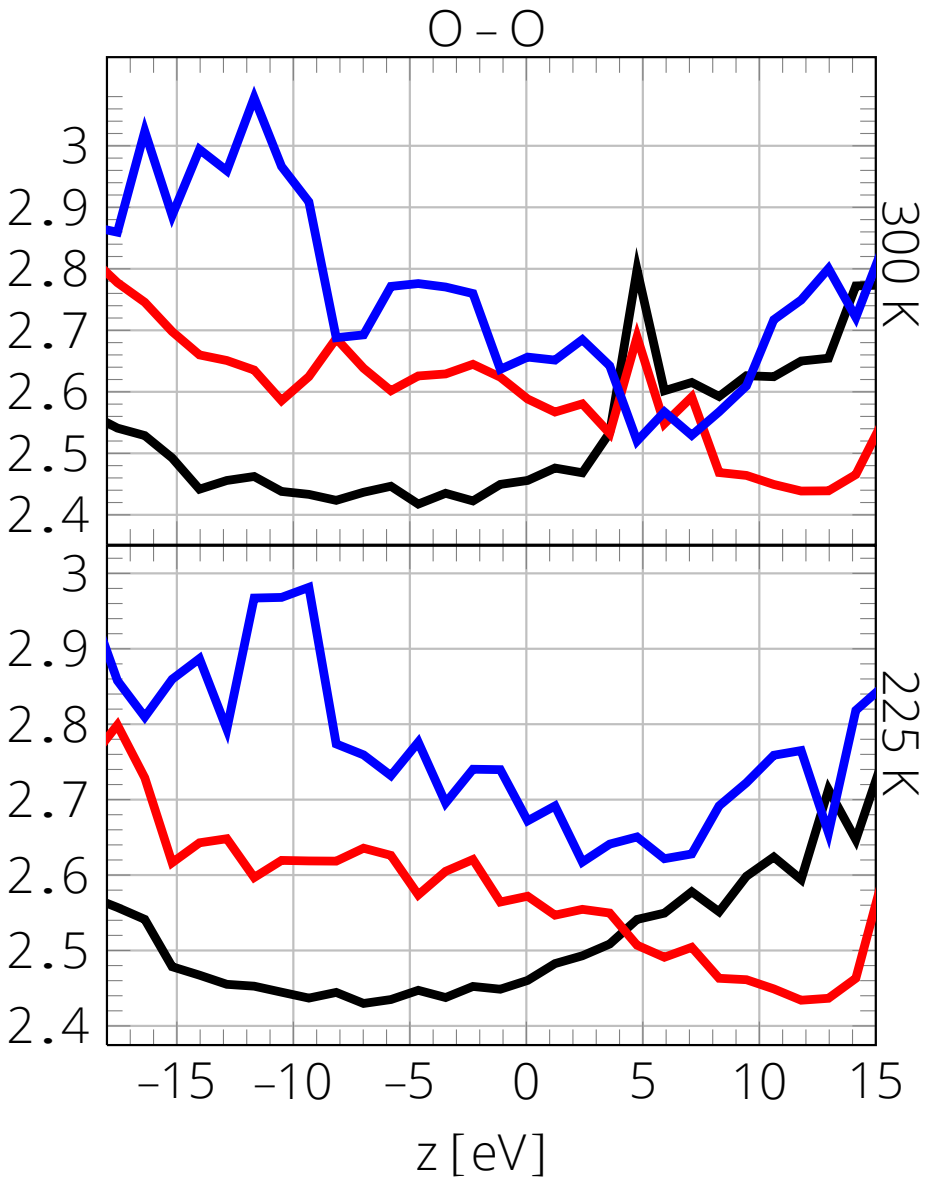
Intermediate state



$[H_9O_4]^+$



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



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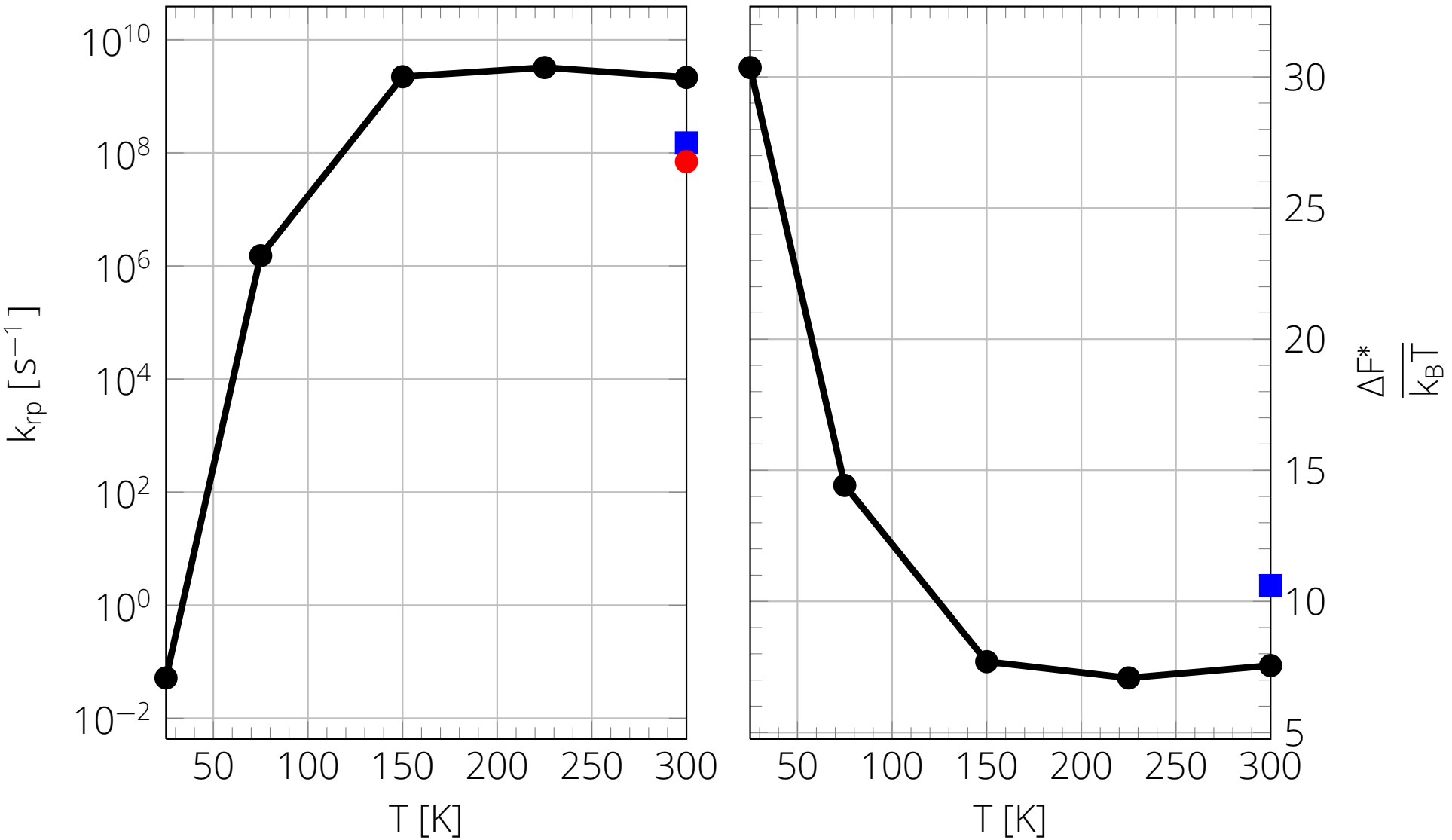
Reaction rate constant



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

Acknowledgements

Giovanni and Simone

Q&A