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HF Dissociation in Water Clusters by Computer Simulations*

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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
Motivation

Acid dissociation

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

carbon cycle

biological systems

\[\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3\]

\[\text{HCO}_3^- \rightarrow \text{H}_3\text{O}^+\]
Motivation

HF dissociation

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

S. Odde et al., *J. Phys. Chem. A*, 2006, **110**, p. 7918
Dissociation of HF in $\text{HF}(\text{H}_2\text{O})_7$

Motivation

Objectives

- Equilibrium constant
- Reaction mechanism
- Reaction rate constant
#### Outline

1. Motivation

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Collective Variables

Description of a process by collective variables

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

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

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

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

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

\[ U_k(x, z) = U(x) + \frac{k}{2} (\theta(x) - z)^2 \]
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Restrainted hybrid Monte Carlo

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

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

$$\delta \mathcal{H}_a = \mathcal{H}_a(x^{i+1}, p^{i+1}) - \mathcal{H}_a(x^i, p^i)$$

$$\mathcal{H}_a(x, p) = U_k(x, z) + K(p)$$

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

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Rate constant calculation

\[
\begin{align*}
\dot{n}_r(t) &= -k_{rp} n_r(t) + k_{pr} n_p(t) \\
\dot{n}_p(t) &= k_{rp} n_r(t) - k_{pr} n_p(t)
\end{align*}
\]

\[
N_r + N_p \approx 1
\]

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

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

\[
k_{rp} = \frac{\nu}{2N_r}
\]

\[
k_{pr} = \frac{\nu}{2N_p}
\]

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

TST with dynamical corrections

\[ \nu = \int \mathrm{d}x \mathrm{d}v \, \dot{\theta}(x) \xi_p(x, v) \xi_r(x, -v) \rho(x, v) \delta(\theta(x) - z^*) \]

\[ = \frac{\int \mathrm{d}x \mathrm{d}v \, \dot{\theta}(x) \xi_p(x, v) \xi_r(x, -v) \rho(x, v) \delta(\theta(x) - z^*)}{\int \mathrm{d}x \mathrm{d}v \, \rho(x, v) \delta(\theta(x) - z^*)} \int \mathrm{d}x \mathrm{d}v \, \rho(x, v) \delta(\theta(x) - z^*) \]

\[ = \left\langle \dot{\theta}(x) \xi_p(x, v) \xi_r(x, -v) \right\rangle_z \, e^{-\beta F(z^*)} \]

- \( \xi_p(x, v) \) 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 \((x, -v)\)

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

\[ \dot{\theta}(x_i(t = 0)) = \frac{\theta(x_i(\delta t)) - \theta(x_i(-\delta t))}{2\delta t} \]
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Collective variable for acid dissociation
Collective variable for acid dissociation

\[ \langle \mathcal{H}_{\text{KS}} \rangle_\alpha = \langle w_\alpha | \mathcal{H}_{\text{KS}}(x) | w_\alpha \rangle \]
\[ \langle \mathcal{H}_{\text{KS}} \rangle_\zeta = \langle w_\zeta | \mathcal{H}_{\text{KS}}(x) | w_\zeta \rangle \]
\[ w_\chi(r) = \sum_i c_{\chi,i}\phi_i(r) \]

\[ \xi_i(x) = \langle \mathcal{H}_{\text{KS}} \rangle_\zeta - \langle \mathcal{H}_{\text{KS}} \rangle_\alpha \]
\[ \xi_i < 0 \text{ covalent bond at } \alpha \]
\[ \xi_i > 0 \text{ covalent bond at } \zeta \]

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

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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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Equilibrium Constant

$pK_a$

\[ K_a = \frac{P_p}{P_r} \quad pK_a = -\log K_a \]

Graph showing the relationship between $pK_a$ and temperature ($T$) with two different conditions: cluster (comp.) and bulk (exp.).
Contributions to the free energy

\[ \Delta F / T \Delta S [\text{eV}] \]

- \[ \Delta F \]
- \[ \Delta E \]
- \[ T \Delta S \]

\[ T [\text{K}] \]

HF Dissociation in Water Clusters...
Equilibrium Constant

\[ S_{\text{h-vib}} = \sum_{i=1}^{N_m} \left\{ \frac{\beta \hbar \nu_i e^{-\frac{\beta \hbar \nu_i}{2}}}{1 - e^{-\frac{\beta \hbar \nu_i}{2}}} - \ln \left( 1 - e^{-\frac{\beta \hbar \nu_i}{2}} \right) \right\} \]
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Results

Mechanism of the Reaction

Mean path

\[ x(z) = \langle x \rangle_z \]
Results

Mechanism of the Reaction

Hydrogen bond chain length

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

Graph showing the hydrogen bond chain length at different temperatures (T=25 K, T=75 K, T=150 K, T=225 K, T=300 K). The graph plots L(z) in Å vs. z in eV. The variation in L(z) with temperature is observed.
Results

Mechanism of the Reaction

\[ \xi_i \text{ VS } z \]

\[ \xi_i(x) = \langle \mathcal{H}_{KS} \rangle_z - \langle \mathcal{H}_{KS} \rangle_{\alpha} \]

Graph showing the change in energy \( \xi_i(x) \) with respect to \( z \) at different temperatures: 300 K, 225 K, 150 K, and 75 K. The graph includes curves for different reactions:
- F - H - O_1
- O_1 - H - O_2
- O_2 - H - O_3

HF Dissociation in Water Clusters...
Results

Mechanism of the Reaction

Intermediate state

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Results

Reaction Rate Constant

Reaction rate constant

$T [K]$

$k_{rp} [S^{-1}]$

$\Delta F^* / k_B T$


We studied dissociation reaction of HF in water clusters by using statistical mechanics of rare events combined with \textit{ab initio} MD.

RhMC was implemented in CP2K.

We developed a CV which is able to monitor and steer the reaction without any strong \textit{a priori} knowledge of the mechanism.

HF is a stronger acid in cluster than in bulk.

HF gets a strong acid at lower T.
Weak acidity of HF has an entropic origin

Negative $\Delta S$ 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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