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<td>Elena, Alin Marin</td>
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HF Dissociation in Water Clusters by Computer Simulations*

Alin M Elena
School of Physics
Scoil na Fisice

Principal supervisor: Prof. Giovanni Ciccotti
Supervisor: Dr. Simone Meloni

University College Dublin
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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 Constant
Acid dissociation

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

carbon cycle

CO₂

atmosphere

CO₂ + H₂O \rightleftharpoons H₂CO₃

H₂O

water

H₂CO₃

chemical weathering

HCO₃⁻, H₃O⁺

rock

biological systems
Motivation

HF dissociation

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

Motivation

Dissociation of HF in HF(H$_2$O)$_7$

Objectives

- Equilibrium constant
- Reaction mechanism
- Reaction rate constant
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Description of a process by collective variables

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

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

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

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

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

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

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

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

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

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


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Rate constant calculation

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

\[
N_r + N_p \approx 1
\]

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

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

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

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

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

TST with dynamical corrections

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

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

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

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

Collective Variable
Collective variable for acid dissociation
Collective variable for acid dissociation

\[
\langle \mathcal{H}_{KS} \rangle_{\alpha} = \langle w_{\alpha} \mid \mathcal{H}_{KS}(x) \mid w_{\alpha} \rangle \\
\langle \mathcal{H}_{KS} \rangle_{\zeta} = \langle w_{\zeta} \mid \mathcal{H}_{KS}(x) \mid w_{\zeta} \rangle \\
w_{\chi}(r) = \sum_{i} c_{\chi,i} \phi_{i}(r)
\]

\[
\xi_{i}(x) = \langle \mathcal{H}_{KS} \rangle_{\zeta} - \langle \mathcal{H}_{KS} \rangle_{\alpha}
\]

\[
\xi_{i} < 0 \text{ covalent bond at } \alpha \\
\xi_{i} > 0 \text{ covalent bond at } \zeta
\]

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

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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 ≈ 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 $300 \text{ K}$
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   - **Equilibrium Constant**
   - Mechanism of the Reaction
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Free energy profile

Equilibrium Constant

Results

$F(z)$ [eV]

$z$ [eV]

$T=25$ K  $T=75$ K  $T=150$ K  $T=225$ K  $T=300$ K

$F(z) / k_B T$
Results

Equilibrium Constant

\[ K_a = \frac{\mathcal{P}_p}{\mathcal{P}_r} \quad \text{pK}_a = -\log K_a \]

Graph showing the relationship between temperature (T [K]) and \( \text{pK}_a \) with data points for cluster (comp.) and bulk (exp.).
Contributions to the free energy

\[ \Delta F / \Delta E / T \Delta S \] [eV]

\( T \) [K]

\( 25 \ 50 \ 75 \ 100 \ 125 \ 150 \ 175 \ 200 \ 225 \ 250 \ 275 \ 300 \)

\( \Delta F \)

\( \Delta E \)

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

Mechanism of the Reaction

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Results

Mechanism of the Reaction

Mean path

\[ x(z) = \langle x \rangle_z \]
Hydrogen bond chain length

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

- \( T = 25 \text{ K} \)
- \( T = 75 \text{ K} \)
- \( T = 150 \text{ K} \)
- \( T = 225 \text{ K} \)
- \( T = 300 \text{ K} \)
Mechanism of the Reaction

\[ \xi_i(\mathbf{x}) = \langle \mathcal{H}_{KS} \rangle \zeta - \langle \mathcal{H}_{KS} \rangle \alpha \]

\[ \xi_i(\mathbf{x}) = \langle \mathcal{H}_{KS} \rangle \zeta - \langle \mathcal{H}_{KS} \rangle \alpha \]

- \( F - H - O_1 \)
- \( O_1 - H - O_2 \)
- \( O_2 - H - O_3 \)

HF Dissociation in Water Clusters...
Results

Mechanism of the Reaction

Intermedi...
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   - Reaction Rate Constat
Results

Reaction Rate Constant

Reaction rate constant

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.
Acknowledgements

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