Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Supporting Information for

# Adsorption of $CO_3^{2-}$/$HCO_3^-$ on the Quartz Surface: Cluster Formation, pH Effects, and Mechanistic Aspects

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**Table S1**. Number of $Na^+$, $HCO_3^-$, $CO_3^{2-}$, and water molecules for each quartz surface system

| | Concentration (M) | $CO_3^{2-}$ | $HCO_3^-$ | $Na^+$ | Water |
|---|---|---|---|---|---|
| **pH = 7.5** | 0.07 | 0 | 6 | 14 | 4355 |
| | 0.14 | 0 | 12 | 20 | 4327 |
| | 0.28 | 0 | 24 | 32 | 4274 |
| **pH = 9.5** | 0.07 | 1 | 5 | 23 | 4346 |
| | 0.14 | 2 | 10 | 30 | 4315 |
| | 0.28 | 4 | 20 | 44 | 4260 |
| **pH = 11** | 0.07 | 5 | 1 | 43 | 4325 |
| | 0.14 | 10 | 2 | 54 | 4294 |
| | 0.28 | 20 | 4 | 76 | 4241 |

**Table S2**. Number of $Na^+$, $HCO_3^-$ and $CO_3^{2-}$ adsorbed on the quartz surface system

| | Concentration (M) | $CO_3^{2-}$ | $HCO_3^-$ | $Na^+$ |
|---|---|---|---|---|
| **pH = 7.5** | 0.07 | 0 | 0.5 | 3.89 |
| | 0.14 | 0 | 1.44 | 5.59 |
| | 0.28 | 0 | 5.4 | 10.75 |
| **pH = 9.5** | 0.07 | 0.3 | 0.29 | 11.76 |
| | 0.14 | 0.89 | 1.56 | 17.84 |
| | 0.28 | 2.4 | 4 | 17.94 |
| **pH = 11** | 0.07 | 3.03 | 0.32 | 33.11 |
| | 0.14 | 7.37 | 0.53 | 39.93 |
| | 0.28 | 10 | 1.2 | 42.58 |

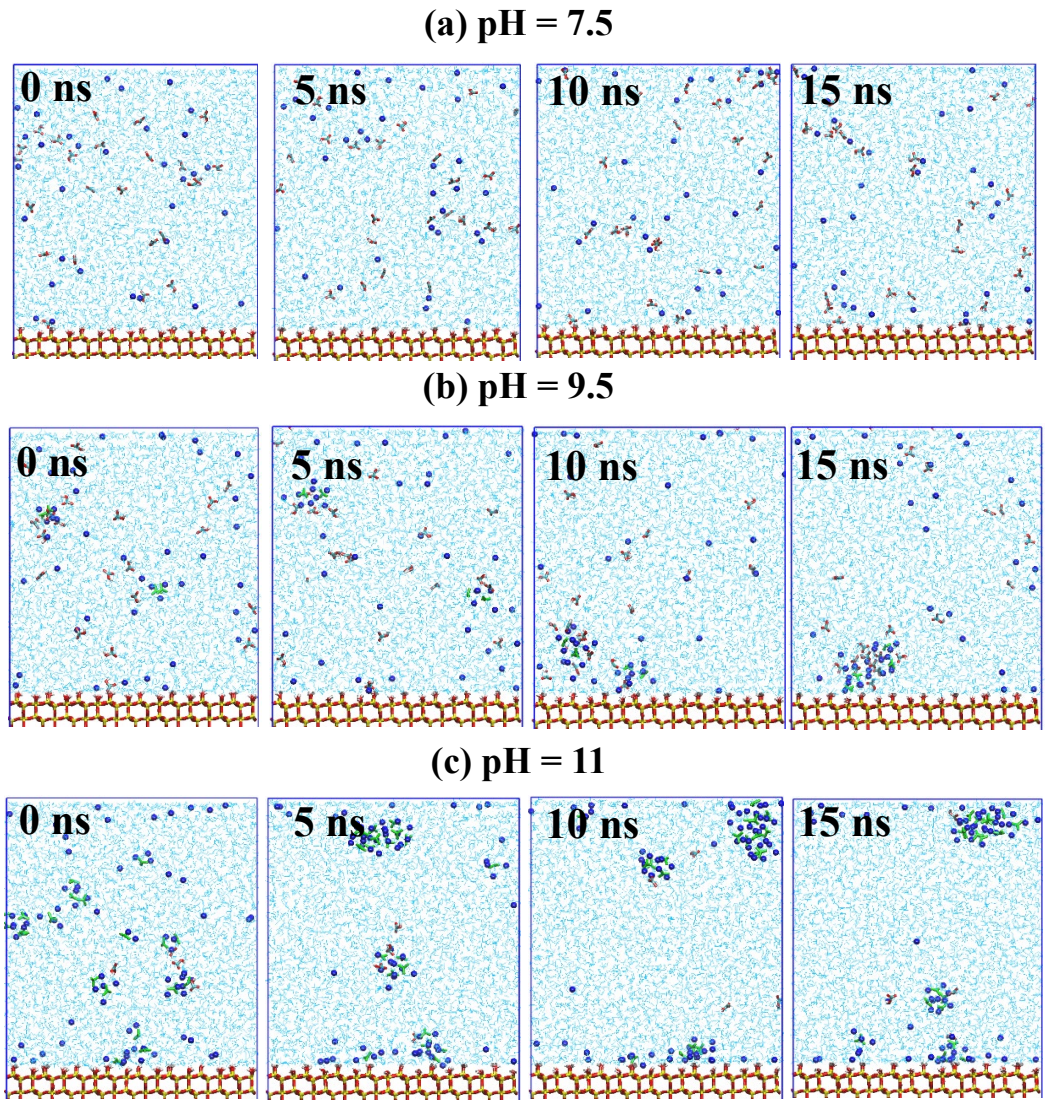


**Figure S1.** Snapshots of cluster evolution with the simulation processes of 0.28 M $NaHCO_3$ and $Na_2CO_3$ solutions at pH = 7.5, 9.5, and 11 interacting with quartz surfaces. (a) for pH = 7.5, (b) for pH = 9.5, and (c) for pH = 11, respectively.

Otherwise noted, the concentration indicates the mole concentration of total carbon fraction in $NaHCO_3$ and $Na_2CO_3$ (The same below). Si, O, H of quartz, Na, and C of $HCO_3^-$ are presented as yellow, red, white, blue, and cyan balls; $CO_3^{2-}$ is presented as green sticks; Water molecules are presented as cyan lines.

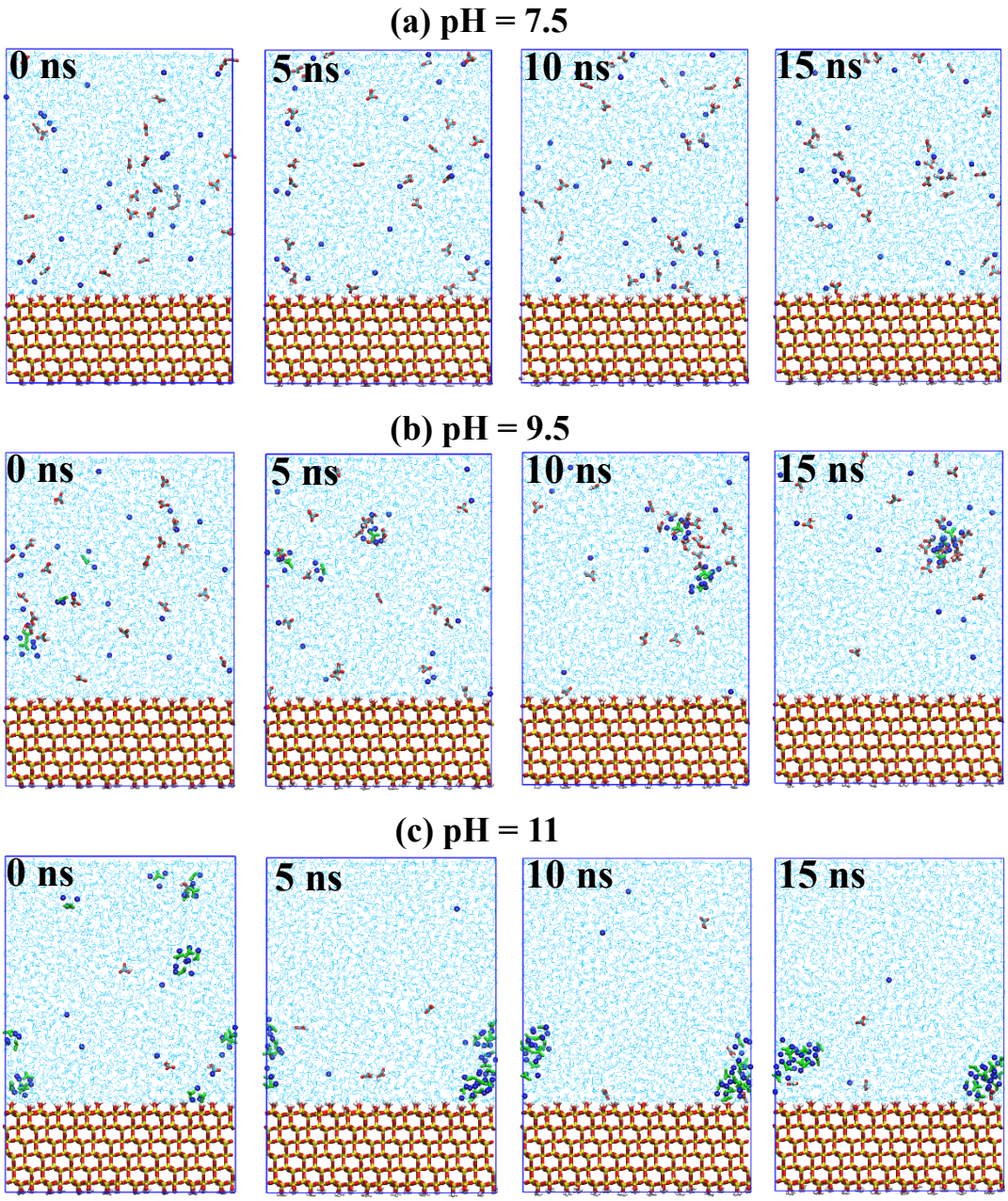


**Figure S2.** Snapshots of adsorption behavior with the simulation processes of 0.28 M $NaHCO_3$ and $Na_2CO_3$ solutions at pH = 7.5, 9.5, and 11 interacting with quartz surfaces. (a) for pH = 7.5, (b) for pH = 9.5, and (c) for pH = 11, respectively. And all quartz surfaces had no charge.

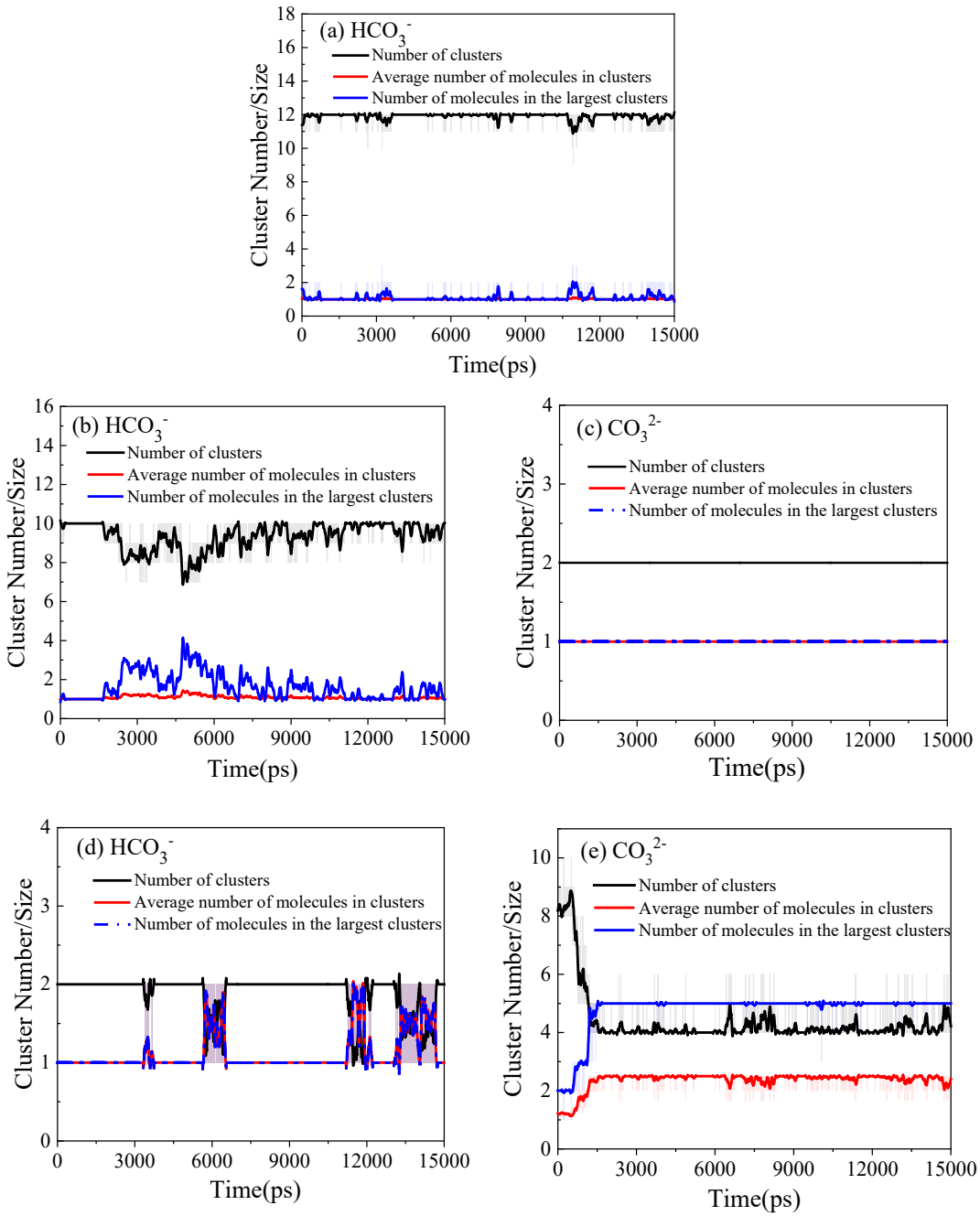


**Figure S3.** Cluster number of $HCO_3^-$ or $CO_3^{2-}$ in 0.14 M carbonate solutions varied with simulation time. (a) for pH = 7.5, (b, c) for pH = 9.5, (d, e) for pH = 11, respectively. Number of clusters, average number of molecules in clusters, and number of molecules in the largest clusters are calculated, respectively.

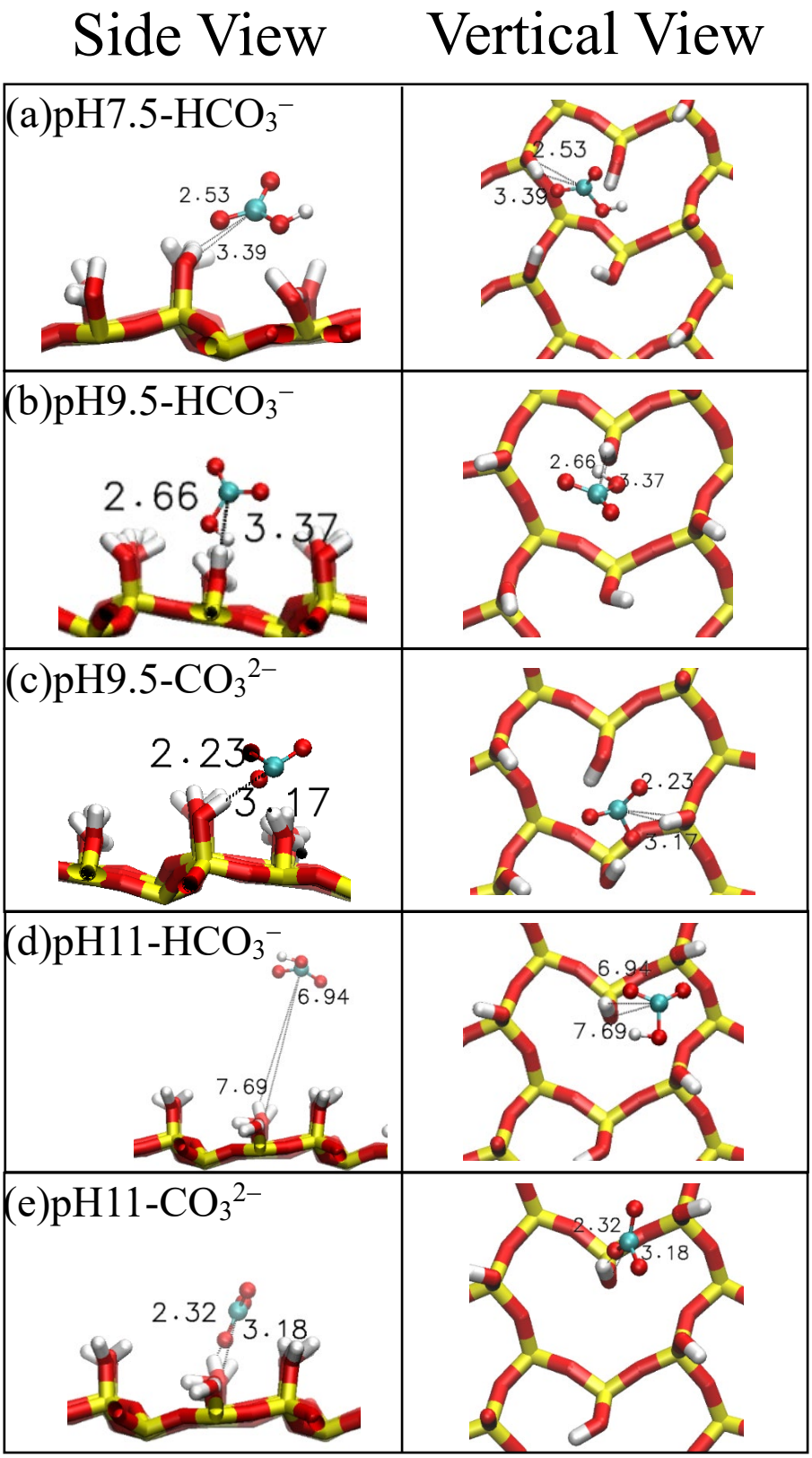


**Figure S4.** The local structures of $HCO_3^-$ (a, b, d) and $CO_3^{2-}$ (c, e) at the quartz surfaces at pH = 7.5 (a), 9.5 (b, c), and 11 (d, e). The concentration of $NaHCO_3$ and $Na_2CO_3$ solution is 0.28 M. a, b, d for $HCO_3^-$ and c, e for $CO_3^{2-}$.

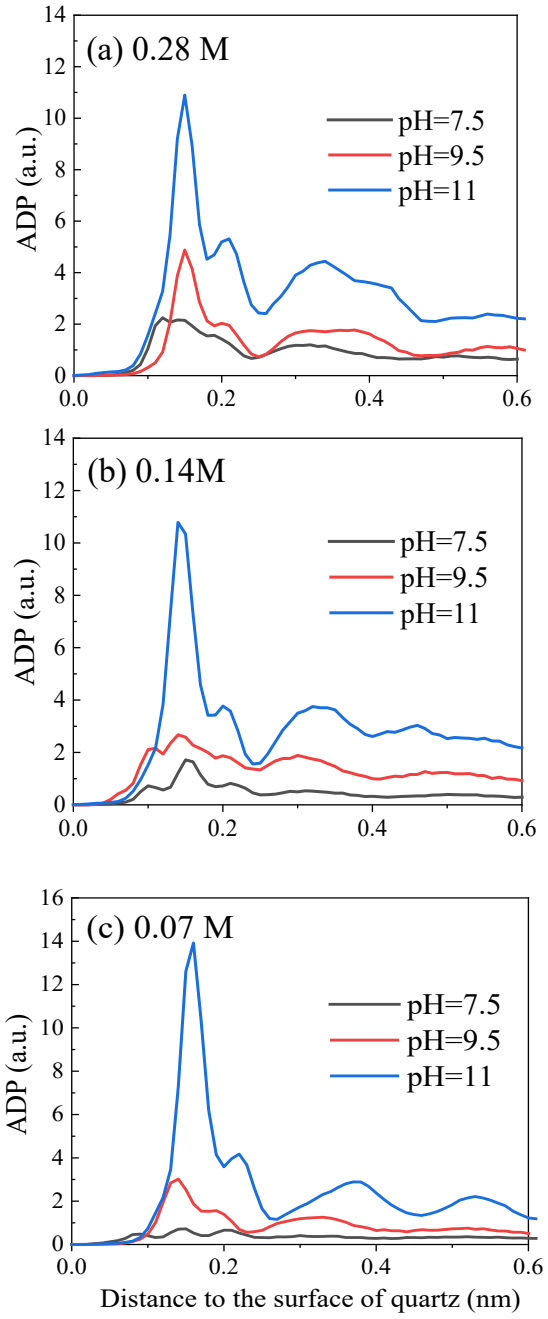


**Figure S5.** Atomic density profiles (ADPs) of $Na^+$ ions normal to the surface of quartz. (a), (b), and (c) correspond 0.28, 0.14, and 0.07 M carbonate solutions, respectively. The pH values are indicated in the legends.

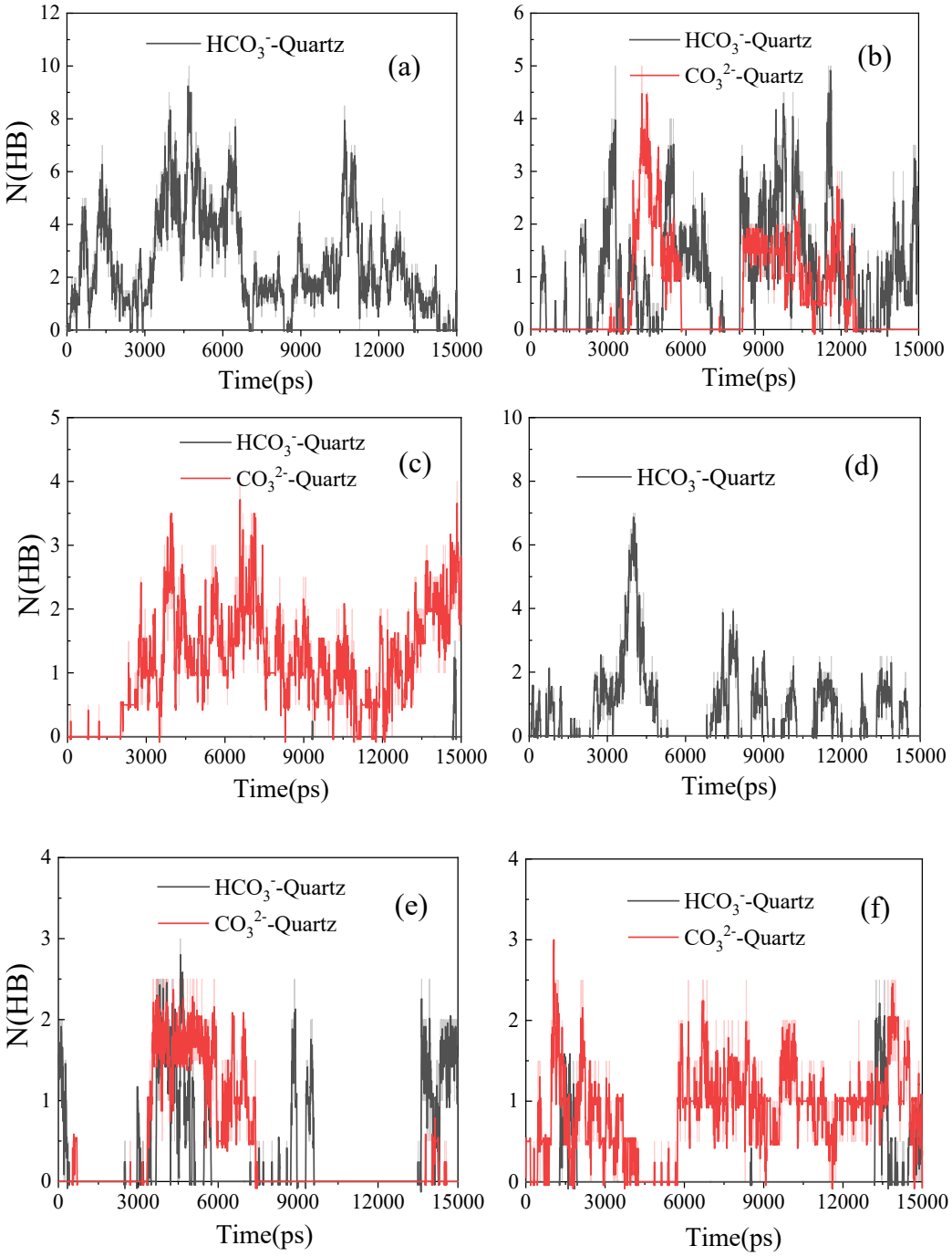


**Figure S6**. Time-evolution number of hydrogen bonds (N(HB)) of the carbonate species $HCO_3^-$ and $CO_3^{2-}$ at 0.14 M (a-c) and the 0.07 M (d-f).

(a, d), (b, e), and (c, f) for pH = 7.5, 9.5, and 11, respectively.