THERMODYNAMIC ANALYSIS OF ELECTRIC FIELD ENHANCED CO$_2$ CAPTURE BY MOISTURE-SENSITIVE QUATERNARY AMMONIUM-BASED SORBENTS

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Climate change incurred by the increasing amount of CO$_2$ released into the atmosphere has become a global priority, and triggers the development of carbon capture, utilization, and storage. Low energy requirement and cost by employing moisture swing process make quaternary ammonium-based materials applicable for CO$_2$ capture. The moisture-sensitive sorbents suffer decreased CO$_2$ affinity and cyclic capacities with moderate or high humidity, while water vapor ubiquitously exists in flue gas or ambient air. The effect of applying electric field on CO$_2$ adsorption, especially the water-involved proton transfer step, by quaternary ammonium-based sorbents in the existence of water, is analyzed. The discrepancy in the hydrophilicity between reactant and product species is enhanced by the electric field, which indicates more favorable chemisorption. Thermodynamics of CO$_2$ adsorption coupling interfacial water evaporation under the electric field are depicted with changes of enthalpy and free energy calculated. Therefore, the rationality of electric field enhanced CO$_2$ capture of quaternary ammonium-based sorbents in moist circumstance is theoretically validated, providing the methodology of optimizing moisture swing adsorption from process intensification apart from material design.

Key words*: CO$_2$ capture; quaternary ammonium; electric field; proton transfer; hydrophilicity*

1. Introduction

The continuous acceleration of global warming have aroused great concern about anthropogenic carbon emissions, propelling the carbon capture, utilization, and storage (CCUS) technologies into deployment [1,2]. As an important part of carbon capture's portfolio, adsorption based on solid materials shows advantages in reduced energy consumption, alleviated equipment corrosion, and resistance to degradation [3,4]. Researches of applying solid materials in capturing CO$_2$ either from the concentrated sources (*e.g.*, flue gas) or the dilute sources (*e.g.*, ambient air) were booming in the past two decade with a variety of sorbents proposed [5-7].

Due to the combined features of ionic liquids and macromolecular structures, polymeric ionic liquids (PILs) are recognized as a series of versatile CO$_2$ sorbents with highly-tunable chemical and physical properties [8]. A specific quaternary ammonium-based PILs whose CO$_2$ affinity influenced

by hydration has been unveiled by Quinn *et al.* When the counteranions come from weak acids such as carbonate and fluoride, the CO_2 adsorption capacity is negatively correlated with humidity. The reaction equilibrium between quaternary ammonium-based materials and CO_2 can be altered by water vapor partial pressure in the atmosphere [9,10]. Based on that property, Lackner and Wang *et al.* proposed the concept of moisture swing sorption, and verified by isothermal CO_2 sorption-desorption tests on the quaternary ammonium-based ion-exchange resins: In a dry environment (*e.g.*, relative humidity<20%), the sorbent with low CO_2 loadings could uptake CO_2 from flue gas or air. The resulting sorbent with high loadings releases CO_2 when exposed to a humid environment (*e.g.*, relative humidity>80%), and is further regenerated by drying to close the capture cycle [11,12].

Compared with solid amine adsorbents which commonly undergo high temperature regeneration [13], moisture swing sorption by quaternary ammonium-based materials can be carried out at room temperature. CO_2 desorption and sorbent regeneration are driven by water evaporation at the gas-solid interface, indicating the potential to greatly reduce energy consumption and cost [14]. However, the inherent moisture-sensitivity of quaternary ammonium sorbent, *i.e.*, the attenuation of CO_2 capacity when the partial pressure of water vapor is excessively high, limits its application in wet environment (such as the saturated flue gas or moist air). By doping hydrophobic carriers such as polyvinylidene difluoride (PVDF) in the heterogeneous synthesis [15] or inserting hydrophobic fragments directly into the polymer chains in the homogeneous synthesis [16], enhancement in the material's hydrophobicity could mitigate the moisture sensitivity to a certain extent though at the expense of CO_2 capacity. Molecular-atomic scale simulations reveal that the core of moisture swing sorption is the proton transfer of interfacial water molecules, and the active hydroxide ions produced provide a strong alkaline environment for CO_2 reaction [17]. The proton transfer process is inhibited under high humidities and its efficient reinforcement is considered to be the breach of tackling the moisture sensitivity [18,19].

It has been demonstrated that the external electric field could play the similar role as a catalyst or inhibitor at will by changing the reaction thermodynamics and kinetics, and thus control the reaction mechanisms [20,21]. Effects of electric field on the proton transfer, especially for the water involved-reactions, have been investigated by quantum chemical methods. Zhou *et al.* found that the proton transfer within H_3N-HCl or H_2O-HCl Lewis acid-base pairs can be driven by external electric field or electrons [22], instead of excess water molecules as revealed by spectroscopic experiments [23]. Only when the field strength applied along the direction of N-H or O-H bond axis reaches a critical value can the proton transfer occur, and the degree of proton transfer can be adjusted by modulating the field strength. Bai *et al.* revealed that electric field can affect the hydrogen bonds which serve as pathways for proton transfer between water molecules. When the field strength exceeds a critical value, the proton transfer is triggered and the proton can transit continuously along the direction of the hydrogen bond, and finally form water whiskers with positive and negative charges at both ends [24].

When exposed to humid atmosphere, strong hydrogen bonds form between the quaternary ammonium cation-anion ion pairs and hydrated water molecules [17]. The changes of hydrogen bonds and hydrated ion pairs in the electric field might further lead to changes of CO_2 reactivity. So far the research objects of proton transfer under the influence of electric field are mainly small molecules with highly symmetrical topologies [20-24]. For the asymmetric and complex system composed of

quaternary ammonium cation with different counteranions and hydration states, how to establish the electric field, *e.g.*, rational selection of direction and strength, and the mechanism of electric field's effect on the hydrogen bonding, proton transfer and CO_2 reaction remains to be investigated.

Herein, we have explored the microscopic mechanism of CO_2 adsorption on moisture-sensitive quaternary ammonium-based materials under the action of electric field by using density functional theory (DFT) calculations. The degree of proton transfer in the hydrated ion pairs after applying electric field is systematically investigated with the function of electric field revealed. The distribution of hydrated water molecules in the presence of electric field is depicted and the evolution of interfacial hydrophilicity/hydrophobicity under different hydration conditions is obtained. The thermodynamic processes and key parameters of CO_2 adsorption and hydration are clarified under selected electric field, and the underlying mechanism of electric field's promotion on CO_2 binding ability in humid atmosphere is interpreted.

2. Computational methods

Considering the cost and accuracy of calculation when the electric field is applied, the chemical structure of quaternary ammonium-based materials is rationally simplified into ion pairs consisting quaternary ammonium cation and its countering anion [17]. Two cases of hydroxide and carbonate as the counteranions are considered in constructing model compound of reactant, which both results into bicarbonate as the couteranion in model compound of product, as shown in fig. 1. Besides, to reflect the rigid feature of solid polymer in model compound of quaternary ammonium-carbonate ion pairs, the distance between two nitrogen atoms in cations is optimized as 7.783 Å in a zero electric field and kept constant in further optimization with electric field [25,26].
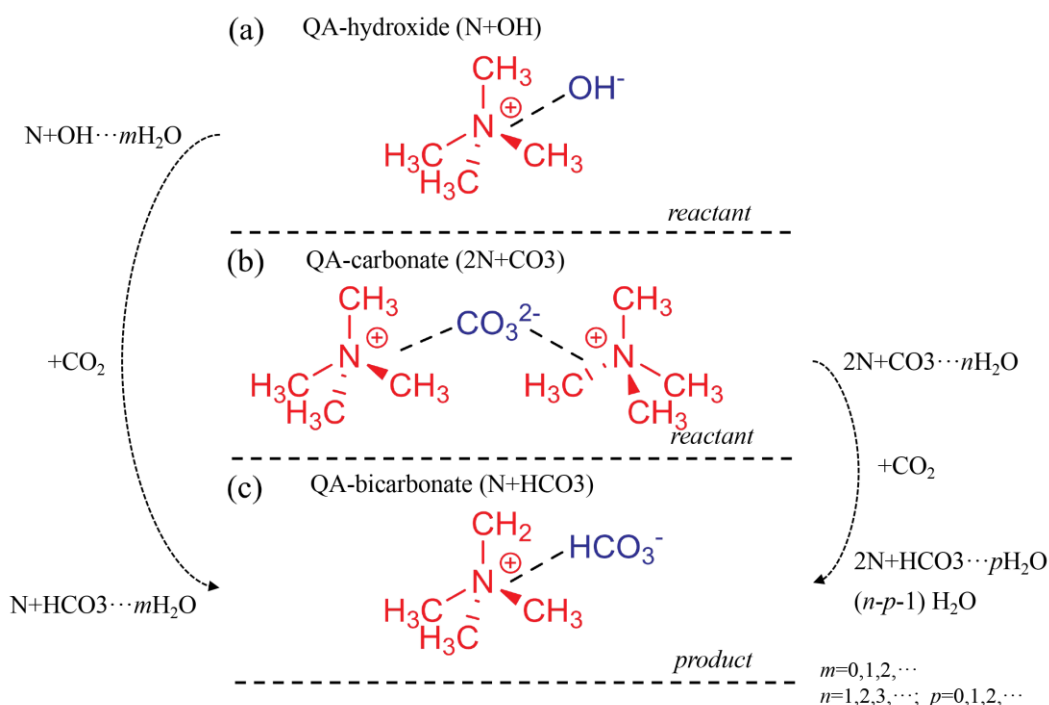

Figure 1. The model compound of QA-hydroxide (a), QA-carbonate (b), and QA-bicarbonate (c) ion pairs, respectively. The schemes of CO_2 reaction are depicted

All the DFT calculations were performed on Gaussian09 software package using the Becke three-parameter Lee-Yang-Parr exchange-correction functional (B3LYP) together with the 6-311++G** basis set [17,27]. The geometries were optimized in a zero electric field and electric filed of different strengths up to 200 a.u. (atomic unit, 1 a.u.=5.142×10^9V/cm) [28]. Single-point energy values were calculated based on the optimized geometry, and the hydrogen bond related energy values were corrected through the counter-poise procedure with basis set superposition errors (BSSEs) [29]. The vibrational frequencies of the optimized geometry were calculated to confirm the minimum state instead of saddle point on the potential energy surface.

The CO_2 adsorption energy of QA-hydroxide (N+OH) can be calculated as eq. 1.

$$E_{ad}(E) = E_{N+OH}(E) + E_{CO2}(E) - E_{N+HCO3}(E) \tag{1}$$

Where $E_{ad}(E)$ denotes the CO_2 adsorption energy in the presence of electric field (E). $E_{N+OH}(E)$, $E_{CO2}(E)$, and $E_{N+HCO3}(E)$ denote the energy of QA-hydroxide ion pair, the energy of CO_2 molecule, and the energy of QA-bicarbonate ion pair in the presence of electric field, respectively [30].

The CO_2 adsorption energy of QA-carbonate (2N+CO3) can be calculated as eq. 2.

$$E_{ad}(E) = E_{2N+CO3}(E) + E_{CO2}(E) - E_{2N+CO3+CO2}(E) \tag{2}$$

Where $E_{2N+CO3}(E)$ and $E_{2N+CO3+CO2}(E)$ denote the energy of QA-carbonate ion pair and the energy of complex comprising QA-carbonate ion pair and CO_2 molecule in the presence of electric field.

The hydration energy of QA-anion (N+A) in the presence of can be calcualted as eq. 3.

$$E_{hyd,n}(E) = E_{N+A...(n-1)H2O}(E) + E_{H2O,n}(E) - E_{N+A...nH2O}(E) \tag{3}$$

Where $E_{hyd,n}(E)$ denotes the hydration energy of QA-anion ion pair when the nth (n=1, 2, 3) H_2O molecule is involved. $E_{N+OH...(n-1)H2O}(E)$ and $E_{N+OH...nH2O}(E)$ denote the energy of QA-anion ion pair with (n-1) and n hydrated H_2O molecule, respectively. $E_{H2O,n}(E)$ denotes the energy of the nth H_2O molecule. The anions refer to hydroxide, carbonate, or bicarbonate.

The Gibbs free energy change of hydration reaction can be calculated as eq. 4.

$$\Delta G^0_{hydn}(E) = \Delta_f G^0_{N+A...nH2O}(E) - (\Delta_f G^0_{N+A...(n-1)H2O}(E) + \Delta_f G^0_{H2On}(E)) \tag{4}$$

Where $\Delta G^0_{hyd,n}(E)$ denotes the Gibbs free energy change when the nth (n=1, 2, 3) H_2O molecule was involved in the hydration of QA-anion ion pairs. $\Delta_f G^0_{N+A...(n-1)H2O}(E)$ and $\Delta_f G^0_{N+A...nH2O}(E)$ denote the Gibbs free energy change of formation of QA-anion ion pair with (n-1) and n hydrated H_2O molecule, respectively. $\Delta_f G^0_{H2O,n}(E)$ denotes the Gibbs free energy change of the nth H_2O molecule.

The enthalpy change and Gibbs free energy change of the overall reaction concerning CO_2 adsorption and interfacial hydration can be calculated as eq. 5 and eq. 6, respectively.

$$\Delta_r H^0(E) = \sum_{pro} \Delta_f H^0(E) - \sum_{rea} \Delta_f H^0(E) \qquad (5)$$

$$\Delta_r G^0(E) = \sum_{pro} \Delta_f G^0(E) - \sum_{rea} \Delta_f G^0(E) \qquad (6)$$

Where $\Delta_r H^0(E)$ and $\Delta_r G^0(E)$ denote the enthalpy change of the overall reaction, respectively. $\sum_{pro} \Delta_f H^0(E)$ and $\sum_{pro} \Delta_f G^0(E)$ denote the enthalpy change of formation and Gibbs free energy change of formation of the product species, respectively. $\sum_{rea} \Delta_f H^0(E)$ and $\sum_{rea} \Delta_f G^0(E)$ denote the enthalpy change of formation and Gibbs free energy change of formation of the reactant species, respectively.

3. Results and discussion

3.1. Characteristics of proton transfer of hydrated carbonate ion in the presence of electric field

It was revealed in previous studies that the CO_2-active sites in the QA-carbonate ion pairs are centered on the anions. Proton is prone to transfer from hydrated water to the carbonate, forming highly-active hydroxide to react with CO_2 [17]. Electric field is introduced along the direction of initial O-C bond axis where oxygen and carbon are from hydrated water and carbonate, respectively. The variations of O-H bond length in the hydrated water and the hydrogen bond length between hydrated water and carbonate under electric field with different strengths are depicted in fig. 2. As the
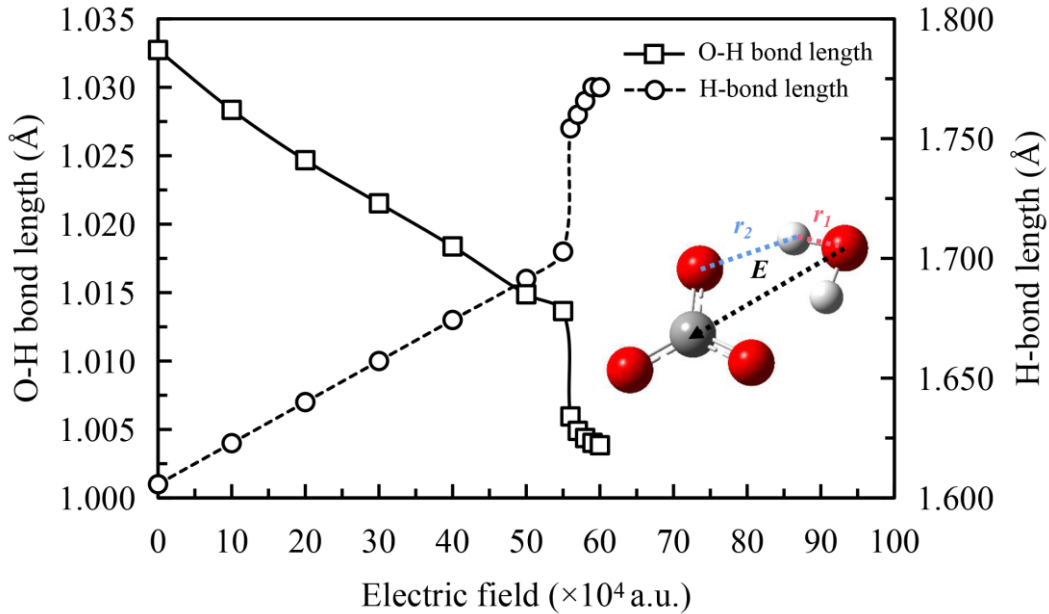

Figure 2. The variation of O-H and hydrogen bond lengths under electric field with different strengths. The selected O-H bond in the hydrated water molecule is the "active" O-H bond with the most drastic change in bond length. The hydrogen bond is between the hydrated water and carbonate ion

electric field strength ranging from 0 to 0.005 a.u., the O-H bond length increases from 1.001 to 1.018 Å and the hydrogen bond length decreases from 1.787 to 1.678 Å. Therefore the enhanced degree of proton transfer can be inferred, and the linear change of O-H or hydrogen bond lengths indicates that

precise controlling the degree of proton transfer can be achieved by adjusting electric field strength. The O-H and hydrogen bond lengths drastically change when the electric field strength exceeds a critical value of 0.0055 a.u., as the O-H bond breaks and proton transfer occurs [22]. The variation of O-H and hydrogen bond lengths becomes mild as the field strength increasing after the critical value.

3.2. Characteristics of proton transfer of hydrated quaternary ammonium-carbonate ion pair in the presence of electric field

The most stable geometry of hydrated QA-carbonate ion pair (I_1) is shown in fig. 3. At first, we proposed that the proton transfer occurs along the original O-H bond axis, where the oxygen and hydrogen atoms are from carbonate and water, respectively. When applying an electric field along the

Most-stable geometry I_1, $E=0$

Meta-stable geometry I_2, $E=0$
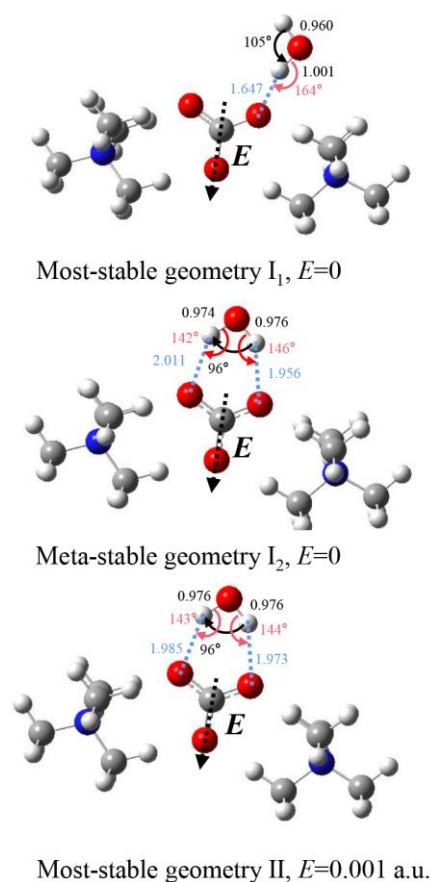
Most-stable geometry II, $E=0.001$ a.u.

Figure 3. The most stable, meta-stable geometries of hydrated QA-carbonate ion pairs in zero electric field, and the most stable geometry of hydrated QA-carbonate ion pair under electric field of 0.001 a.u.

O-H direction, the ion pair rotates, making the O-H bond deviating from the field's direction and C-O bond in the carbonate parallel to the field's direction. Therefore, the electric field is set along the direction of original C-O bond axis to rationally constrain the geometry change in the optimization. Introducing an electric field of 0.001 a.u. results in high symmetry in the field's direction (II). We surmises that with the perturbation from electric field, the most stable but asymmetrical geometry (I_1) easily transforms into another stable and symmetrical geometry (I_2), whereas the energy of latter is

slightly higher (0.4 kJ/mol). The meta-stable geometry (I_2) is used as reference for zero electric field in the following calculation.

The "active" O-H bond length, the hydrogen bond length, and the NPA (Natural Population Analysis) charge of the oxygen atom in the hydrated water molecule under different electric field strengths are depicted in fig. 4, respectively. Similar to the simple case of hydrated carbonate ion, the intensified degree of proton transfer is revealed as sudden change of O-H and hydrogen bond lengths around the critical field strength of 0.0124 a.u., with the slopes changing from 1.2 to 290 Å/a.u. and -12.3 to -1950 Å/a.u. for O-H and hydrogen bond, respectively. The negative charge of oxygen atom in the hydrated water molecule increases with field strength, *e.g.*, the negative charges of oxygen atom are 0.913 and 1.093 without electric field and with electric field of 0.015 a.u. The enhanced basicity deduced from the 19.7% increment in the electronegativity of the oxygen atom also suggests that electric field could benefit the reaction with CO_2 [17]. The differential charge distributions due to electric field are depicted in fig. 5, and a general trend of electron density transfer along the negative direction of C-O bond can be revealed.
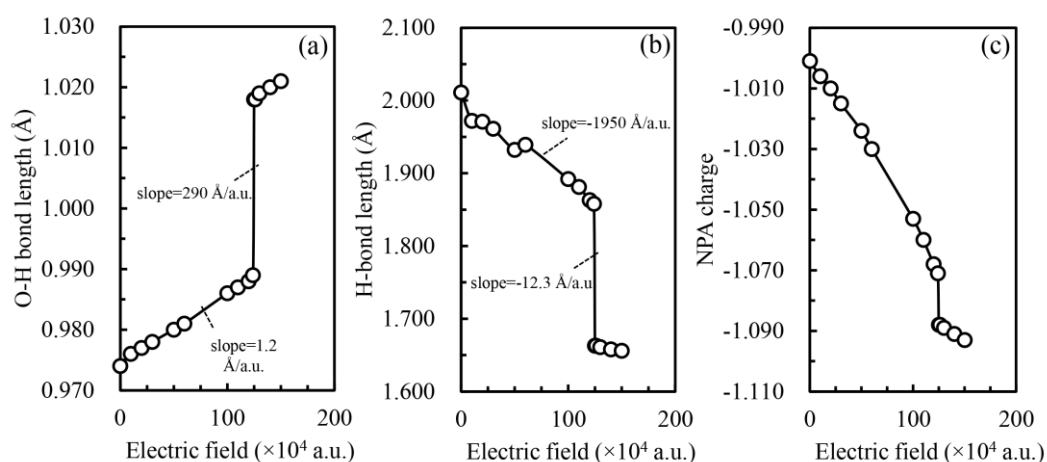

Figure 4. The "active" O-H bond length (a), the hydrogen bond length (b), and the NPA charge of the oxygen atom in the hydrated water (c) under different electric field strengths
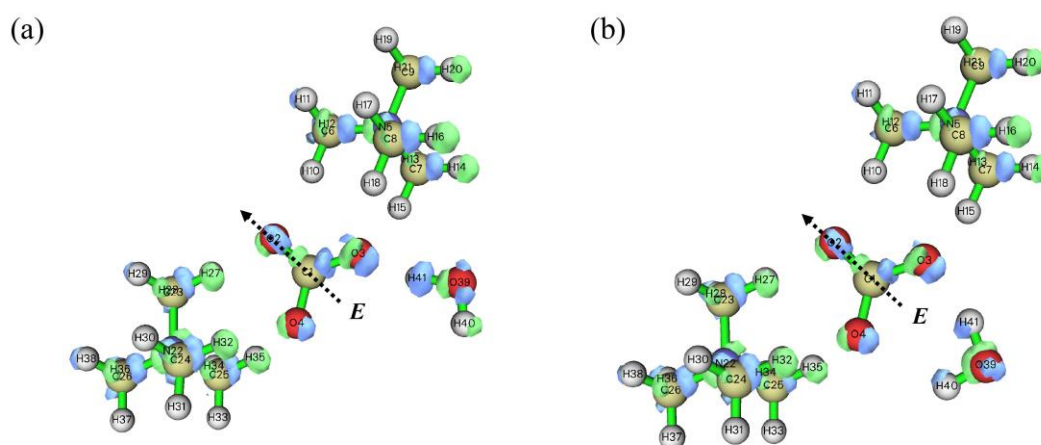

Figure 5. The differential charge distributions when the electric field increasing from zero to 0.015 a.u. (a) and from 0.001 a.u. to 0.015 a.u. (b), respectively. Regions with increased and decreased electron density are marked in green and blue, respectively

3.3. Characteristics of CO_2 interaction with quaternary ammonium-hydroxide/carbonate ion pairs in the presence of electric field

Figure 6 illustrates the change of potential energy of reactant complex comprising QA-hydroxide ion pair and CO_2 molecule with the distance between the CO_2 molecule and hydroxide. In the absence of electric field, the potential energy of reactant complex relative to QA-bicarbonate ion pair monotonously decreases to zero, showing no transition state, as the reaction of CO_2 and hydroxide is one-step with high kinetics [17]. The CO_2 adsorption energy calculated (85.4 kJ/mol) indicates a typical chemi-sorption process [31]. Introducing an electric field along the direction of C-O bond axis where carbon and oxygen are from CO_2 and hydroxide results in a more steep decline curve of the potential energy with CO_2-hydroxide distance. The CO_2 adsorption energy could increase to 182.6 kJ/mol with electric field strength of 0.01 a.u., while the electrostatic interaction between QA and bicarbonate is weaken. We postulate that an electric field not exceeding 0.01 a.u. might be preferred in order to modulate and enhance the CO_2 binding ability.
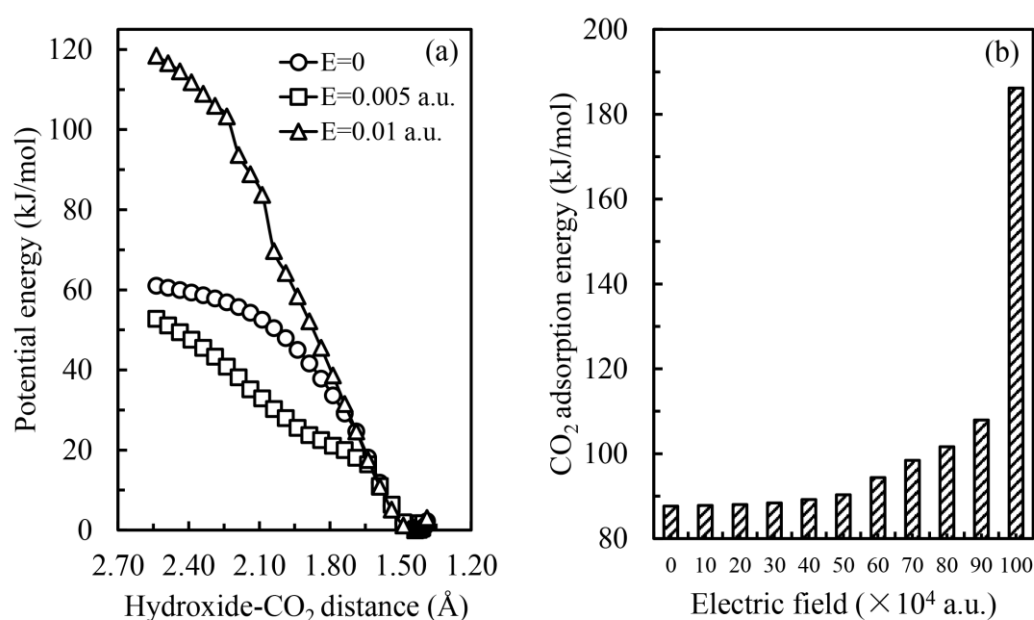

Figure 6. (a) The change of potential energy of reactant complex with the distance between the CO_2 molecule and hydroxide under different electric field strengths. The distance is measured from the coordinates of carbon and oxygen atoms. The energy of optimized QA-bicarbonate ion pair is selected as the reference. (b) The CO_2 adsorption energy of QA-hydroxide ion pair under different electric field strengths

The optimized geometry of complex comprising QA-carbonate ion pair and CO_2 is shown in fig. 7. The CO_2 adsorption energy of QA-carbonate ion pair is 35.9 kJ/mol, reflecting a physi-sorption feature [32]. Once a directional electric field is introduced, the selected C-O bond in QA-carbonate ion pair becomes parallel to the field's direction after optimization. Therefore, the field's direction is fixed along the initial C-O bond axis to constrain the geometry change and speed up the convergence as well. An electric field of 0.005 a.u. along the direction of C-O bond axis could induce a 14% increment in adsorption energy and a 36% increment in dipole moment of CO_2 molecule. Flipping the direction of

the field but keep the same strength, the CO_2 adsorption energy was reduced by 22% to 27.9 kJ/mol, *i.e.*, the direction of electric field can be adjusted to impart the selectivity of electric field on promoting or weakening the physical CO_2 adsorption by the QA-carbonate ion pair [20]. Based on this property an electric field-motivated CO_2 adsorption-desorption process could be designed. A similar role of electric field plays in CO_2 physi-sorption on *h*-BN boron nitride was discovered by Guo *et al* [26].
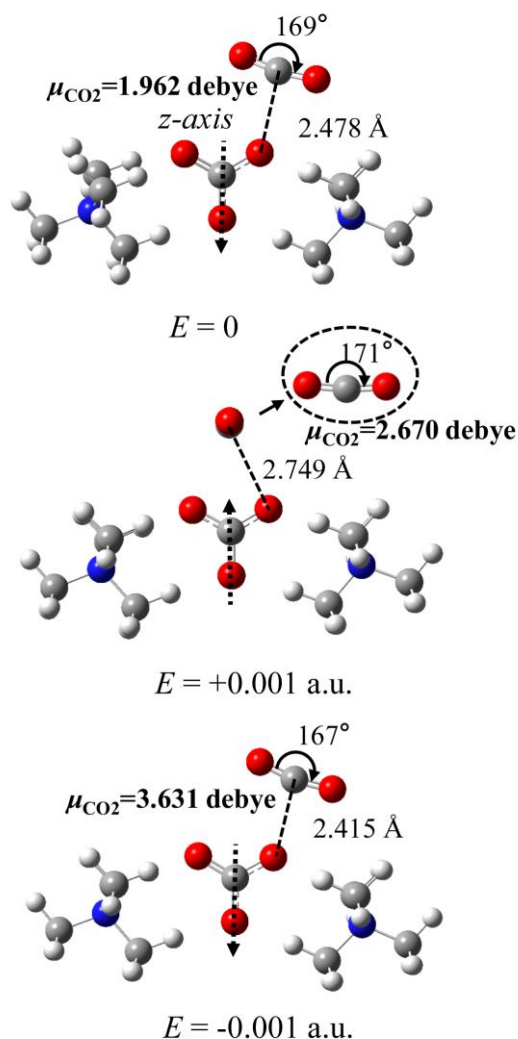

Figure 7. The optimized geometry of QA-carbonate ion pair and CO_2 complex in the presence of electric field

3.4. Characteristics of hydration reaction of quaternary ammonium-hydroxide/carbonate ion pairs in the presence of electric field

The hydration reaction of quaternary ammonium-based materials, especially the difference in hydration energies between reactants and products, is fundamental in determining the thermodynamic properties of moisture swing adsorption. The parameters of the optimized geometries for reactant model compounds (QA-hydroxide, QA-carbonate) and product model compound (QA-carbonate) under electric field are tabulated in tab. 1. In the presence of electric field, an overall trend of increase

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in the O-H bond length and decline in the hydrogen bond length emerges, reflecting the enhancement of hydrophilicity of the QA-hydroxide/carbonate ion-pairs by electric field, while the trend of the product model compound is opposite, with the hydrated water molecule further away from the QA-bicarbonate ion-pair in the presence of electric field showing the hydrophobicity [34].

Table 1. The effect of electric field on the bond length of "active" O-H bond in the hydrated water (r_1), the bond length of hydrogen bond forming between and anions and the hydrated water molecule (r_2), and the NPA charge of oxygen atom in the hydrated water molecule (q_{oxy}) under different hydration states. The results without applying electric field are presented in parentheses for comparison.

		r_1 [Å]	r_2 [Å]	q_{oxy}
	$n_w=1$	1.033(1.021)	1.536(1.595)	-1.021(-1.027)
QA-hydroxide	$n_w=2$	1.020(1.012)	1.568(1.623)	-1.019(-1.016)
	$n_w=3$	1.033(1.019)	1.533(1.580)	-1.039(-1.024)
	$n_w=1$	0.980(1.001)	1.935(1.647)	-1.027(-1.004)
QA-carbonate	$n_w=2$	1.016(0.995)	1.601(1.670)	-1.011(-1.000)
	$n_w=3$	1.011(1.000)	1.634(1.684)	-1.006(-1.012)
	$n_w=1$	0.990(0.995)	1.740(1.691)	-0.997(-1.004)
QA-bicarbonate	$n_w=2$	0.986(0.981)	1.780(1.793)	-0.992(-1.001)
	$n_w=3$	0.990(0.990)	1.739(1.716)	-0.978(-1.017)

To describe the hydration activity and CO_2 reactivity of the quaternary ammonium-based materials in ultra humid atmosphere, the high hydration state ($n_w=3$) is selected and the optimized configuration of hydrated QA-hydroxide/carbonate/bicarbonate ion pairs under an electric field of 0.005 a.u. is shown in fig. 8. In the presence of electric field, water molecules around the carbonate remains uniformly distributed, but the cluster radius (R_{TH}) increases from 4.377 Å to 4.690 Å, reflecting the weakened hydrogen bond within the water molecules themselves and the enhanced hydrogen bond with the QA-carbonate ion pair. On the contrary, the electric field might strengthen the hydrogen bond within water molecules around the hydroxide as the R_{TH} of water clusters decreasing from 4.528 Å to 4.146 Å. In the absence of electric field, the R_{TH} of the bicarbonate-bound water molecules is 3.768 Å. The phenomenon of water molecules deviating from the anionic region reflects the dominant hydrogen bonding within the hydrated water clusters, and R_{TH} is scaled down by 9.4% under the influence of electric field to 3.414 Å, showing strong hydrophobicity at the product interface [34,35]. It is thus evident that the difference between the reactant and product at the hydrophilic level can further be amplified in the presence of electric field, especially for the QA-carbonate ion pair.
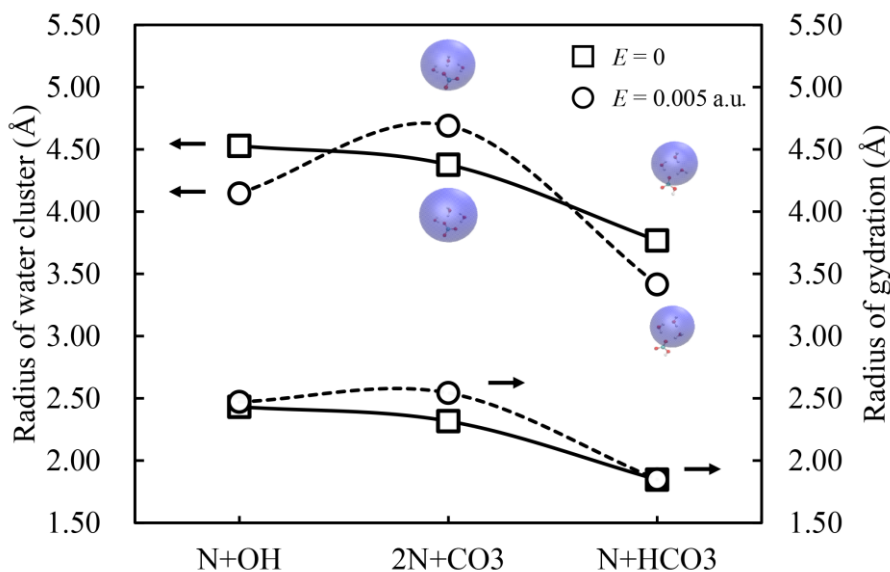
Figure 8. The influence of electric field on the distribution of hydrated waters. R_{TH}, R_{geo}, R_{vdW}, and Rg (Å) are the radii of water cluster, the geometrical radius of water cluster, the van der Waals radius of the atoms at the edge of water cluster, and the radius of gyration of water cluster, respectively. R_{TH} is the sum of R_{geo} and R_{vdW}. The common-used indicator of molecule size, R_g, is also given for comparison.

The effects of electric field on the hydration energies and the Gibbs free energy changes of hydration of the reactant and product model compounds are shown in fig. 9. The hydration energies of the reactant model compounds are higher than those of the product model compounds in zero electric field, *e.g.*, the hydration energies of the QA-hydroxide and QA-carbonate ion pairs are higher than those of the QA-bicarbonate ion pairs by 13.3 and 12.1 kJ/mol, respectively, when the number of hydrated water (n_w) equals 1. However, the difference in the hydration energies shows a tendency of decreasing as n_w increasing.

The hydration energies of QA-carbonate and quaternary ammonium-hydroxide ion pairs are increased by 4.3-47.2 kJ/mol after the application of an electric field of 0.005 a.u, and the gain of the electric field is more significant for the low hydration state. The increase in the absolute value of the Gibbs free energy change of the reaction also corroborates the facilitation of hydration by the electric field. Whereas, the changes in the hydration energy of the QA-bicarbonate ion pair only varies in the range of -4.3-11.9 kJ/mol under electric field of the same field strength. For the hydration process whose n_w increasing from 1-2 and 2-3, the hydration energies of QA-hydroxide and QA-bicarbonate ion pairs before and after the CO_2 reaction increase from 2.8 kJ/mol and 1.2 kJ/mol in the absence of electric field to 25.3 kJ/mol and 12.3 kJ/mol in the presence of electric field, respectively. The structural and thermodynamic parameters obtained from above calculations indicate that the electric field helps to maintain the hydrophilic-hydrophobic discrepancy between the product and reactant at high ambient humidity, which consequently improves the CO_2 adsorption performance of quaternary ammonium based-materials.
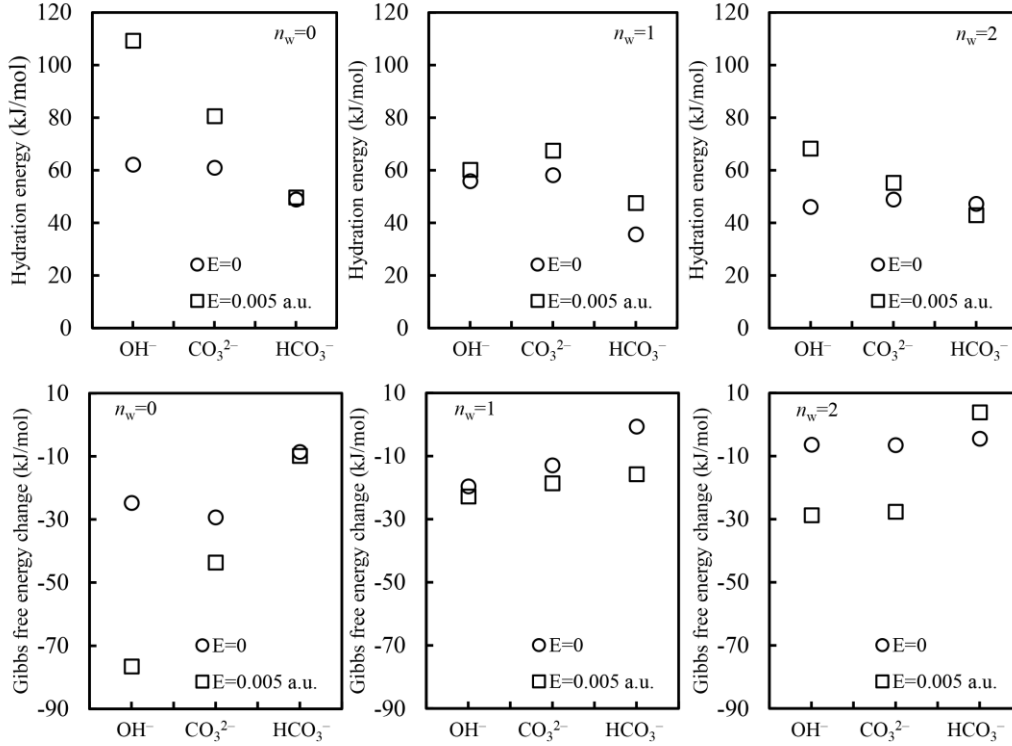
Figure 9. The influence of electric field on the hydration energies and the Gibbs free energy changes for different hydration stages (n_w=0-1, 1-2, 2-3)

3.5. Characteristics of CO_2 reaction thermodynamics with hydrated quaternary ammonium-hydroxide/carbonate ion pairs in the presence of electric field

The reaction of QA-hydroxide ion pair with CO_2 can be carried out under bone dry conditions, and the CO_2 adsorption energy decreases from 85.4 to 53.5 kJ/mol with interfacial hydration (n_w=1), which is attributed to the decrease in the alkalinity of the system due to the migration of the negative charge of hydroxide to hydrated water molecule [17]. Under hydrated conditions, the CO_2 adsorption energy is increased by 43.9% to 77.0 kJ/mol after applying an electric field of 0.005 a.u. along the direction of C-O bond axis, and the CO_2 binding ability is restored to a state comparable to that of the non-hydrated condition, which shows that the introduction of an electric field effectively improves the CO_2 reactivity of QA-hydroxide ion pairs in humid environment.

For the QA-carbonate ion pair, classical thermodynamic theory and molecular simulation have delineated the release of hydrated water molecules accompanying the CO_2 adsorption, with the lumped reaction described in the following equation [14]:

$$[NR_4^+]CO_3^{2-}[NR_4^+] \cdot a H_2O_{(ad)} + CO_2 \rightarrow 2[NR_4^+]HCO_3^- \cdot b H_2O_{(ad)} + (a-b-1)H_2O_{(g)} \quad (7)$$

Where a and b are the number of hydrated water for QA-carbonate ion pair, QA-bicarbonate ion pair, respectively. The suffix $_{(ad)}$ and $_{(g)}$ denotes the adsorbed and gaseous states, respectively.

Given the reaction occurs under ideal hydration conditions (*a>b*, *a* an *b* are integers), the reaction enthalpies and Gibbs free energy changes of CO_2 adsorption and interfacial hydration are listed in tab. 2. The lumped reaction enthalpy gradually changes from negative to positive with the increase of hydrated water release in zero electric field, indicating that the reaction changes from an exothermic to endothermic process, which is in consistency with the spontaneous cooling adsorption reported by Wang *et al* [34]. Under low hydration state (*a=1*), the migration of hydrated water is not significant, and the heat release could increase from 16.7 to 79.0 kJ/mol with 0.005 a.u. electric field introduced. Under high hydration state, the spontaneous cooling effect is somewhat inhibited by the electric field, and the heat uptake decreases from 41.5 to 14.5 kJ/mol when *a=3* and *b=1*, which may be attributed to the differed functions of electric field on the non-polar molecules (*e.g.*, CO_2) and the polar molecules (*e.g.*, H_2O) [20].

When no electric field is applied, the Gibbs free energy changes of CO_2 adsorption coupled with interfacial hydration are positive or small negative in the highly hydrated state (*a=3*), and the positive spontaneity of the CO_2 reaction is very weak, which corresponds to the moisture sensitivity of the quaternary ammonium-based material. After the intervention of electric field, the Gibbs free energy changes of the three cases (*a-b-1=0, 1, 2*) are all negative (-41.3~-21.8 kJ/mol), and the CO_2 adsorption can still be carried out spontaneously in the high hydration state. The above simulation results demonstrate that the rational design of the electric field can improve the CO_2 adsorption performance of quaternary ammonium-based materials under high humidity from the thermodynamic point of view.

Table 2. Thermodynamic parameters of the lumped CO_2 adsorption reaction under ideal hydration conditions

E (a.u.)	*a*	*b*	ΔH_r (kJ/mol)	ΔG_r (kJ/mol)	*a-b*-1
0	1	0	-16.7	-10.6	0
0.005	1	0	-79.0	-88.3	0
0	2	0	41.5	2.4	1
0	2	1	-7.4	-6.2	0
0.005	2	0	-1.3	-59.5	1
0.005	2	1	-51.0	-69.3	0
0	3	0	90.3	8.8	2
0	3	1	41.5	0.3	1
0	3	2	-7.4	-8.3	0
0.005	3	0	64.2	-21.8	2
0.005	3	1	14.5	-31.5	1
0.005	3	2	-35.2	-41.3	0

4. Conclusion

In this paper, the effect of applying electric field on the interfacial hydration and CO_2 adsorption of moisture-sensitive quaternary ammonium-based materials was investigated by quantum chemistry modelling. The main conclusions are as follows:

a. For the QA-hydroxide ion pair, CO_2 adsorption is a one step reaction without energy barriers. Electric field intervention could modulate the interaction of CO_2 with the interface, thus adapting to the requirements of CO_2 capture from sources with differed partial pressure. Under high hydration conditions, the electric field can effectively improve the adsorption capacity weakened by water vapor.

b. For the QA-carbonate ion pair, the magnitude and direction of electric field can be adjusted to strengthen or weaken the physical adsorption of the ion pair with CO_2 under unhydrated conditions, and the electric field-driven adsorption-desorption process can be designed under the high partial pressure accordingly, *i.e.*, under the hydration conditions, the core step of the QA-carbonate ion pair reacting with CO_2, proton transfer, can be controlled by the electric field. The critical field strengths required for the proton transfer of hydrated carbonate and hydrated QA-carbonate ion pair are 0.0055 a.u. and 0.0124 a.u., respectively.

c. The hydrophilicity of the QA-hydroxide and QA-carbonate reactant ion pairs can be enhanced and the hydrophilicity of the QA-bicarbonate product ion pair can be simultaneously reduced by reasonably manipulating the electric field. The discrepancy in the hydration energies of the reactants and the products can be increased from 2.8 to 25.3 kJ/mol and 1.2 to 12.3 kJ/mol, for hydroxide and carbonate cases respectively, with an electric field of 0.005 a.u. introduced.

d. Rational design of electric field has a promoting effect on CO_2 adsorption in high humidity environment. After applying an electric field of 0.005 a.u., the Gibbs free energy change of the adsorption reaction, which is extremely weak in positive spontaneity, can be changed from -8.3~8.8 kJ/mol to -41.3~-21.8 kJ/mol. It significantly improves the moisture sensitivity of the quaternary ammonium based material for CO_2 adsorption in the thermodynamic point of view.

References

[1] Bui, M., *et al.*, Carbon capture and storage (CCS): The way forward, *Energy and Environmental Science*, *11* (2018), 5, pp. 1062-1176

[2] Johnsson, F., *et al.*, The importace of CO_2 capture and storage - A geopolitical discussion, *Thermal Science*, *16* (2012), 3, pp. 655-668

[3] Wang, Q., *et al.*, CO_2 capture by solid adsorbents and their applications: Current status and new trends, *Energy and Environmental Science*, *4* (2011), 1, pp. 42-55

[4] DeWitt, S., *et al.*, Critical comparison of structured contactors for adsorption-based gas separations, *Annual Review of Chemical and Biomolecular Engineering*, *9* (2018), pp. 129-152

[5] Raganati, F., *et al*., Adsorption of Carbon Dioxide for Post-combustion Capture: A Review, *Energy and Fuels*, *35* (2021), 16, pp. 12845-12868

[6] Zhu, X., *et al*., Recent advances in direct air capture by adsorption, *Chemical Society Reviews*, *51* (2022), 15, pp. 6574-6651

[7] Hou, C. L., *et al*., Study on the roles of water in solid amine-based direct air capture of CO_2, *The 9th International Conference on Energy Materials and Environment Engineering*, Kuala Lumpur, Malaysia, 2023, Vol. 406, pp. 02042

[8] Mecerreyes, D., Polymeric ionic liquids: Broadening the properties and applications of polyelectrolytes, *Progress in Polymer Science*, *36* (2011), 12, pp. 1629-1648

[9] Quinn, R., *et al*., Salt Hydrates: New Reversible Absorbents for Carbon Dioxide, *Journal of the American Chemical Society*, *117* (1995), 1, pp. 329-335

[10] Quinn, R., Ion Exchange Resins as Reversible Acid Gas Absorbents, *Separation Science and Technology*, *38* (2003), 14, pp. 3385-3407

[11] Lackner, K. S., Capture of carbon dioxide from ambient air, *The European Physical Journal Special Topics*, *176* (2009), 1, pp. 93-106

[12] Wang, T., *et al*., Moisture Swing Sorbent for Carbon Dioxide Capture from Ambient Air, *Environmental Science & Technology*, *45 (*2011), 15, pp. 6670-6675

[13] Liu, W., *et al*., Analysis on temperature vacuum swing adsorption integrated with heat pump for efficient carbon capture, *Applied Energy*, *335* (2023), pp. 120757

[14] Wang, T., *et al*., Moisture-swing sorption for carbon dioxide capture from ambient air: a thermodynamic analysis, *Physical Chemistry Chemical Physics*, *15* (2013), 2, pp. 504-514

[15] Dong, H., *et al*., Humidity sensitivity reducing of moisture swing adsorbents by hydrophobic carrier doping for CO_2 direct air capture, *Chemical Engineering Journal*, *466* (2023), pp. 143343

[16] Hou, C. L., *et al*., Porosity and hydrophilicity modulated quaternary ammonium-based sorbents for CO_2 capture, *Chemical Engineering Journal*, *413* (2021) pp. 127532

[17] Wang, T., *et al*., Theoretical studies on CO_2 capture behavior of quaternary ammonium-based polymeric ionic liquids, *Physical Chemistry Chemical Physics*, *18* (2016), 18, pp. 13084-13091

[18] Xiao, H., *et al*., The catalytic effect of H_2O on the hydrolysis of CO_3^{2-} in hydrated clusters and its implication in the humidity driven CO_2 air capture, *Physical Chemistry Chemical Physics*, *19* (2017), 40, pp. 27435-27441

[19] Shi, X., *et al*., Capture CO_2 from Ambient Air Using Nanoconfined Ion Hydration, *Angewandte Chemie International Edition*, *55* (2016), 12, pp. 4026-4029

[20] Shaik, S., *et al*., Oriented electric fields as future smart reagents in chemistry, *Nature Chemistry*, *8* (2016), 12, pp. 1091-1098

[21] Stuyver, T., *et al*., External electric field effects on chemical structure and reactivity, *Wiley Interdisciplinary Reviews Computational Molecular Science*, *10* (2020), 2, pp. e1438

[22] Zhou, Z. J., *et al*., Electric Field-Driven Acid-Base Chemistry: Proton Transfer from Acid (HCl) to Base (NH_3/H_2O), *The Journal of Physical Chemistry A*, *115* (2011), 8, pp. 1418-1422

[23] Eustis, S. N., *et al*., Electron-Driven Acid-Base Chemistry: Proton Transfer from Hydrogen Chloride to Ammonia, *Science*, *319* (2008), 5865, pp. 936-939

[24] Bai, Y., *et al*., Electric Field Effects on the Intermolecular Interactions in Water Whiskers: Insight from Structures, Energetics, and Properties, *The Journal of Physical Chemistry A*, *119* (2015), 10, pp. 2083-2090

[25] Elking, D. M., *et al*., A Finite Field Method for Calculating Molecular Polarizability Tensors for Arbitrary Multipole Rank, *Journal of Computational Chemistry*, *32* (2011), 15, pp. 3283-3295

[26] Calvaresi, M., *et al*., Splitting CO_2 with Electric Fields: A Computational Investigation, *The Journal of Physical Chemistry Letters*, *1* (2010), 22, pp. 3256-3260

[27] Arabi, A., *et al*., Effects of external electric fields on double proton transfer kinetics in the formic acid dimer, *Physical Chemistry Chemical Physics*, *13* (2011), 30, pp. 13738-13748

[28] Shaik, S., *et al*., Electric-Field Mediated Chemistry: Uncovering and Exploiting the Potential of (Oriented) Electric Fields to Exert Chemical Catalysis and Reaction Control, *Journal of the American Chemical Society*, *142* (2020), 29, pp. 12551-12562

[29] Boys, S. F., *et al*., The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors, *Molecular Physics*, *19* (1970), 4, pp. 553-566

[30] Jiang, Q. G., *et al*., Reversible Transition of Graphene from Hydrophobic to Hydrophilic in the Presence of an Electric Field, *The Journal of Physical Chemistry C*, *116* (2012), 36, pp. 19321-19326

[31] Didas, S. A., *et al*., Amine-Oxide Hybrid Materials for CO_2 Capture from Ambient Air, *Accounts of Chemical Research*, *48* (2015), 4810, pp. 2680-2687

[32] Dunne, J. A., *et al*., Calorimetric Heats of Adsorption and Adsorption Isotherms. 2. O_2, N_2, Ar, CO_2, CH_4, C_2H_6, and SF_6 on NaX, H-ZSM-5, and Na-ZSM-5 Zeolites, *Langmuir*, *12* (1996), 24, pp. 5896-5904

[33] Guo, H., *et al*., CO_2 Capture on *h*-BN Sheet with High Selectivity Controlled by External Electric Field, *The Journal of Physical Chemistry C*, *119* (2015), 12, pp. 6912-6917

[34] Wang, T., *et al*., Spontaneous Cooling Absorption of CO_2 by a Polymeric Ionic Liquid for Direct Air Capture, *The Journal of Physical Chemistry Letters*, *8* (2017), 17, pp. 3986-3990

[35] Wang, T., *et al.*, Designing Moisture-Swing CO_2 Sorbents through Anion Screening of Polymeric Ionic Liquids, *Energy Fuels*, *31* (2017), 10, pp. 11127-11133