# Ab Initio Thermodynamic Study of the CO<sub>2</sub> Capture Properties of Potassium Carbonate Sesquihydrate, K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O

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ABSTRACT: By combining density functional theory and lattice phonon dynamics, the thermodynamic properties of CO<sub>2</sub> absorption/desorption reactions with dehydrated potassium carbonates through K2CO3·1.5H2O +  $CO_2 = 2KHCO_3 + 0.5H_2O(g)$  are analyzed. The energy change and the chemical potential of this reaction have been calculated and used to evaluate its thermodynamic properties and phase transitions. The results indicate that the K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O can only be applied for postcombustion CO<sub>2</sub> capture technology at temperatures lower than its phase transition temperature, which depends on the CO<sub>2</sub> pressure and the steam pressure with the best range being  $P_{\rm H_2O} \leq 1.0$ bar. Above the phase transition temperature, the sorbent will be regenerated into anhydrous  $K_2CO_3$ . If the steam pressure  $P_{H_2O}$  is much greater than 1.0 bar, it is possible to use the K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O sorbent for precombustion CO<sub>2</sub> capture technology. Compared to anhydrous K<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, 1.5H<sub>2</sub>O requires less energy for regeneration.

# I. INTRODUCTION

Since the burning of fossil fuels is the main energy source for the world economy, carbon dioxide, a major product from fossil fuel combustion, is released into the atmosphere in large quantities and may cause global climate change.<sup>1-5</sup> In order to solve this environmental problem, there is a need to reduce CO<sub>2</sub> emissions through capture and sequestration while maintaining acceptable energy costs.<sup>6-9</sup> During the past few decades, many efforts have been devoted to new technologies for CO<sub>2</sub> capture, sequestration, and utilization.<sup>4,10</sup> Among them, capture is economically the key step, and the use of sorbents to remove CO<sub>2</sub> from large point sources is a feasible capture technology. Inorganic solid sorbent materials have been proposed for capture of  $CO_2$  through a reversible chemical transformation.<sup>1,10-13</sup>

Solid sorbents containing alkali and alkaline earth metals have been reported in the literature.<sup>1,14-18</sup> Their oxides, hydroxides, and carbonates/bicarbonates attract more attention from researchers because of their high  $CO_2$  absorption capacities and moderate working temperatures.<sup>10,14,19,20</sup> Experimental evidence also shows that mixtures of hydroxides with oxides could improve the CO<sub>2</sub> absorption performance.<sup>14</sup> Since alkali metal bicarbonates can be decomposed into carbonates releasing CO2 and H2O within a relatively small temperature range (for example, NaHCO<sub>3</sub> at 70-250 °C), carbonate/bicarbonate conversions can be used for  $CO_2$  capture under postcombustion conditions.<sup>10-15,17,19,21-26</sup> Gen-

erally, a fluidized-bed or transport reactor is imagined for the postcombustion  $CO_2$  capture by alkali metal carbonates.<sup>22,27–30</sup> The flue gas enters the carbonation reactor to react with sorbent in the temperature range of 60-80 °C depending on which carbonate/bicarbonate is used. Then the loaded sorbents are transferred into the regeneration reactor to release CO<sub>2</sub> and regenerate the sorbent in the temperature range 100-200 °C. Lee et al.<sup>11-15,23,31</sup> and Zhao et al.<sup>22,27,29,32,33</sup> investigated pure K<sub>2</sub>CO<sub>3</sub> and potassium-based sorbents (K<sub>2</sub>CO<sub>3</sub>/TiO<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>/  $Al_2O_3$ ,  $K_2CO_3/MgO_1$ ,  $K_2CO_3/ZrO_2$ , etc.) to capture  $CO_2$ through the overall reaction  $K_2CO_3 + CO_2 + H_2O =$ 2KHCO<sub>3</sub>. Their results indicated that the global carbonation rate for  $Na_2CO_3/K_2CO_3$  was rather slow. The results measured by Lee et al.<sup>11,23,28</sup> showed that, within 100 min, the carbonation conversion rate of the potassium-based sorbents reached 80% while for sodium-based sorbents it only reached 65%.<sup>21</sup>

Hirano et al.<sup>34</sup> and Hayashi et al.<sup>35</sup> reported that the formation of active species K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O plays an important role in the CO<sub>2</sub> capture capacity and that a vapor pretreatment process substantially improved the CO<sub>2</sub> capture capacity.<sup>14</sup> The experimental results showed that the CO<sub>2</sub> capture capacity could be enhanced due to the conversion of the K<sub>2</sub>CO<sub>3</sub> phase





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to the K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O phase through the K<sub>4</sub>H<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·1.5H<sub>2</sub>O phase during pretreatment with sufficient water vapor.<sup>14</sup> Shigemoto and Yanagihara<sup>25</sup> proposed potassium carbonate supported on an activated carbon as an efficient sorbent to recover CO<sub>2</sub> from moist flue gas through the reaction K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O + CO<sub>2</sub> = 2KHCO<sub>3</sub> + 0.5H<sub>2</sub>O. However, by using thermogravimetric analysis (TGA) and X-ray diffraction (XRD) measurements to obtain the characteristics of potassium-based sorbents for CO<sub>2</sub> capture, Zhao et al.<sup>22</sup> found that the carbonation reactivity of K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O and K<sub>2</sub>CO<sub>3</sub> (in monoclinic structure and dehydrated from K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O) was weak, but K<sub>2</sub>CO<sub>3</sub> (in hexagonal structure) calcined from KHCO<sub>3</sub> showed excellent carbonation capacity and reproducibility.

Although the thermodynamic properties of  $K_2CO_3$  are wellknown either from databases<sup>36,37</sup> or from our first-principles calculations,<sup>17,18,38</sup> in the literature, there is a lack of thermodynamic data for  $K_2CO_3 \cdot 1.5H_2O$ . In order to evaluate the  $CO_2$  capture performance of  $K_2CO_3 \cdot 1.5H_2O$  and to compare with the corresponding anhydrous  $K_2CO_3$ , in this study we apply our previous approach<sup>16,39,40</sup> to explore the electronic and lattice dynamic properties of  $K_2CO_3 \cdot 1.5H_2O$ crystal. Then, based on the calculated energetic properties, we will calculate the thermodynamic properties of  $CO_2$  capture reactions by  $K_2CO_3 \cdot 1.5H_2O$  and  $K_2CO_3$  to find the optimal working conditions for achieving maximum capture capacity.

The rest of this paper is organized as follows: section II briefly describes the theoretical method employed. Section III presents the results of the electronic structural and phonon properties of  $K_2CO_3$ ·1.5H<sub>2</sub>O compared with the corresponding anhydrous  $K_2CO_3$ . Based on those properties, the thermodynamic properties of reactions of these carbonates in capturing  $CO_2$  are evaluated and their corresponding working conditions are fully analyzed. Section IV contains a brief summary and conclusions.

## **II. THEORETICAL METHODS**

The complete description of our computational methodology can be found in our previous studies.<sup>16–18,38–42</sup> Here, we limit ourselves to provide only the main aspects relevant for the current study. When applying hydrated and dehydrated potassium carbonates as solid  $CO_2$  absorbents, we have the following reactions:

$$K_2CO_3 \cdot 1.5H_2O + CO_2 \stackrel{T,P}{\longleftrightarrow} 2KHCO_3 + 0.5H_2O(g)$$
(R1)

and

$$K_2CO_3 + H_2O(g) + CO_2 \stackrel{T,P}{\longleftrightarrow} 2KHCO_3$$
 (R2)

Assuming the difference between the chemical potentials of solid phases (K<sub>2</sub>CO<sub>3</sub>, KCO<sub>3</sub>·1.5H<sub>2</sub>O, and KHCO<sub>3</sub>) can be approximated by the differences in their electronic energies ( $\Delta E_{\rm DFT}$ ) and their entropies ( $\Delta S_{\rm PH}$ ) and harmonic free energies ( $\Delta F_{\rm PH}$ ), we can obtain the temperature- and pressure-dependent chemical potential ( $\Delta \mu$ ) for the above reactions:<sup>16-18,38-42</sup>

$$\Delta\mu(T, P) = \Delta\mu^{0}(T) - RT \ln\left(\frac{P_{\rm CO_{2}}}{P_{0}} \left(\frac{P_{\rm H_{2}O}}{P_{0}}\right)^{n_{0}}\right)$$
(1)

$$\Delta \mu^0(T) = \Delta E_{\rm DFT} + \Delta E_{\rm ZP} + \Delta F_{\rm PH}(T) - G_{\rm CO_2}(T)$$
$$- n_0 G_{\rm H_2O}(T) \tag{2}$$

where  $\Delta E_{ZP}$  is the zero-point-energy difference between the reactants and products and can be obtained directly from phonon calculations.  $P_0$  is the standard state reference pressure of 1 bar. For reaction R1, the  $n_0$  in eqs 1 and 2 is -0.5, whereas for reaction R2 it is  $n_0 = 1$ . The enthalpy change for reaction R1,  $\Delta H^{cal}(T)$ , can be derived from eqs 1 and 2 as

$$\Delta H^{\rm cal}(T) = \Delta \mu^0(T) + T(\Delta S_{\rm PH}(T) - S_{\rm CO_2}(T) - n_0 S_{\rm H_2O}(T))$$
(3)

As described in our previous study,<sup>16,38-41</sup> the zero-point energies, the free energies, and the entropies of the gas phases of CO<sub>2</sub> ( $E_{zp_{CO_2}}$ ,  $G_{CO_2}(T)$ ,  $S_{CO_2}(T)$ ) and  $H_2O(g)$  ( $E_{zp_{H_2O}}$ ,  $G_{\rm H,O}(T)$ ,  $S_{\rm H,O}(T)$ ) can be obtained by standard statistical mechanics and accurately evaluated using the Shomate equation.<sup>37</sup> In eq 2,  $\Delta E_{\text{DFT}}$  is the total energy change of the reactants and products calculated by density functional theory (DFT). In this work, the Vienna Ab initio Simulation Package  $(VASP)^{43,44}$  was employed to calculate the electronic structures of the solid materials involved in this study. All calculations have been done using the projector augmented wave (PAW) pseudopotentials and the PW91 exchange-correlation functional.<sup>45</sup> This computational level was shown to provide an accurate description of oxide systems.<sup>16,17,40,46</sup> Plane wave basis sets were used with a cutoff energy of 500 eV and a kinetic energy cutoff for augmentation charges of 605.4 eV. The kpoint sampling grids of  $n_1 \times n_2 \times n_3$ , obtained using the Monkhorst–Pack method,<sup>47</sup> were used for these bulk calculations, where  $n_1$ ,  $n_2$ , and  $n_3$  were determined consistent to a spacing of about 0.028  $Å^{-1}$  along the axes of the reciprocal unit cells. The corresponding k-points set that we used in our calculations is  $4 \times 3 \times 6$  for  $K_2CO_3 \cdot 1.5H_2O$ . The valence electrons contain the outer s and p orbitals of H, C, and O atoms, and the outer s, p, and d orbitals of K. During the calculations, all atoms in the cell as well as the lattice dimensions and angles were relaxed to the equilibrium configurations. For band structure and phonon dispersion calculations, the symbols and coordinates of the high symmetry points in the first Brillouin zone of the crystals are taken from Bradley and Cracknell's definitions.<sup>48</sup>

In eqs 2 and 3, the zero-point energies  $(E_{ZP})$ , entropies  $(S_{PH})$ , and harmonic free energies  $(F_{PH})$ , excluding the zeropoint energy which was already counted in the term  $\Delta E_{ZP}$ ) of solids were calculated by the PHONON software package,<sup>49</sup> in which the direct method is applied following the formula derived by Parlinski et al.<sup>50</sup> to combine ab initio DFT with lattice phonon dynamics calculations. In the phonon calculations, a 1  $\times$  1  $\times$  2 supercell is created for K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O from its optimized unit cell that is calculated through DFT. Based on the partition function carried out with the phonon dispersions and phonon densities of states, their thermodynamic properties, such as internal energy, free energy, entropy, and heat capacity, can be evaluated under different temperature and pressure conditions that are used in eq 1 to calculate the chemical potentials for reactions R1 and R2, which are further used to evaluate its CO<sub>2</sub> capture properties as presented in section III.C.

with

## **III. RESULTS AND DISCUSSION**

**III.A. Electronic Structural Properties of K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O.** The original synthesis and crystal structure of potassium carbonate sesquihydrate, K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O, was first reported by Hunter and Jeffrey<sup>51</sup> and further redetermined by Skakle et al.<sup>52</sup> It is monoclinic with space group C2/c (No. 15), and its crystal structure is shown in Figure 1a. From it one can see that the  $CO_3^{2-}$  groups are connected with H<sub>2</sub>O by hydrogen bonding to form a chain structure along (010). O1 of  $CO_3^{2-}$  is not involved in the hydrogen bonding. One water molecule (O4 in Figure 1) participates in hydrogen bonds bridging between O3 atoms of two symmetry-related  $CO_3^{2-}$  anions, whereas the other water (O5 in Figure 1) acts as a donor to both O2 and O3 as shown in Figure 1b.<sup>52</sup> The K atoms are located within the hydrogen-bonded chains with K–O bond lengths around 2.74–3.05 Å.

In Table 1 we summarize the optimized crystal structure parameters of K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O. For comparison, we also list the optimized data for anhydrous  $K_2CO_3^{38}$  and  $KHCO_3^{18}$  in Table 1. As one can see, the optimized crystal constants along the aaxis and *c*-axis are increased by about 3.1 and 1.9% compared to experiment whereas the b-axis dimension is decreased 0.5%. Overall, the optimized crystal structure and volume of K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O are in good agreement with the experimental measurements. In Table 2, we summarize the calculated bond lengths and bond angles as well as the experimentally measured data. The optimized bond lengths and angles in the  $CO_3^{2-}$ anion are very close to the measured data. As pointed out by Ireta et al.,53 the accuracy of DFT for describing hydrogen bonds depends on the bond directionality and, for better accuracy, the hydrogen bond angle should be larger than 130°. As shown in Table 2, the hydrogen bond angles in our K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O calculation are larger than 167° (close to linear), so the hydrogen bonds should be well described by the DFT method we have used. For the hydrogen bonding (O<sub>w</sub>- $H \cdots O'$ ) in  $K_2 CO_3 \cdot 1.5H_2O$ , although the calculated bond lengths of  $O_w$ -O' ( $O_w$  refers to O of H<sub>2</sub>O, O' refers to O2 and O3 of  $CO_3^{2-}$ ) are close to experiment, the bond lengths of O<sub>w</sub>-H and H…O' have a larger discrepancy. A likely reason is that the H position in the XRD measurement was not precisely determined, as the experimentally reported H-O lengths are substantially shorter than expected for a water molecule.

The calculated band structure of K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O is shown in Figure 2. The bandwidths and gaps are listed in Table 3. Comparing with the band structure of anhydrous  $K_2CO_{3}^{3}$ similarities are observed in that both are insulator materials and have direct band gaps with values of 4.298 and 3.697 eV for  $K_2CO_3 \cdot 1.5H_2O$  and  $K_2CO_3$ , respectively. They have several valence bands (VBs), and in both solids around -12 eV the p electrons of K form a single band. However, as described below, K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O has its own special electronic structures. However, as described in our previous work,<sup>39-41,46</sup> due to the DFT approximations, which underestimate the unoccupied orbital energies, our calculated band gap is usually smaller than the experimental measurements. Although there is no experimental band gap available for crystalline K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O, it is expected that the real band gap should be larger than our predicted value.

Figure 3 shows the calculated total density of states (TDOS) and partial density of states (PDOS) projected onto the H, C, O, and K contributions for  $K_2CO_3$ ·1.5H<sub>2</sub>O. For comparison, the TDOS of anhydrous  $K_2CO_3$  is also plotted in Figure 3.<sup>38</sup>







**Figure 1.** (a) Crystal structure of  $K_2CO_3 \cdot 1.5H_2O_3$ ; (b) hydrogenbonded chains formed from water and carbonate groups. The biggest balls in red stand for O, the smallest balls in white stand for H, middle-size balls in gray stand for C, and middle-size balls in purple stand for K. The hydrogen bonds are in yellow.

The s orbital of O contributes to the second lowest energy  $VB_6$  by interacting with the p orbital of C, while its p orbitals mainly contribute to  $VB_1$  and  $VB_2$ . The p orbital of K forms a single valence band ( $VB_5$ ) while its s, p, and d orbitals also are involved in other VBs and the conduction band interacting with

Table 1. Experimental and Optimized Crystal Structural Parameters of K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O, KHCO<sub>3</sub>, and K<sub>2</sub>CO<sub>3</sub>

				experimental structure	opti	nized structure
crystal	space group and ref	N	lattice const (Å)	atomic fractional coord	lattice const and deviations (%)	atomic fractional coord
K2C03-1.5H20	C12/c1 (No. 15) <sup>51,52</sup>	×	a = 11.8175 b = 13.7466 c = 7.1093 $\beta = 120.769^{\circ}$	K: (0.00000, 0.38193, 0.25000) (0.00000, 0.68676, 0.25000) (0.35595, 0.349980, 0.45736) C: (0.1929, 0.17350, 0.15183) O: (0.10641, 0.22728, 0.15315) (0.17704, 0.14186, -0.03042) (0.17704, 0.14186, -0.03042) (0.17704, 0.14186, -0.03042) (0.17704, 0.14186, -0.03042) (0.17410, 0.45866, 0.0838) H: (-0.057, -0.0334, 0.172) (0.114, 0.5148, 0.133) (0.189, 0.445, 0.046)	a = 12.17844 (3.05) b = 13.67275 (-0.54) c = 7.243753 (1.89) $\beta = 120.5247^{\circ} (-0.2)$	K: (0.00000, 0.38210, 0.25000) (0.00000, 0.68668, 0.25000) (0.19381, 0.170529, 0.15174) C: (0.19381, 0.170529, 0.15174) O: (0.10307, 0.22130, 0.14661) (0.29710, 0.15112, 0.33471) (0.18347, 0.13803, -0.02683) O., (0.00000, -0.00860, 0.25000) (0.14759, 0.45805, 0.08582) H: (-0.06974, -0.05520, 0.15616) (0.17381, 0.52755, 0.12836) (0.17381, 0.52755, 0.04821) (0.20930, 0.42802, 0.04821)
KHCO <sub>3</sub> ª	P12 <sub>1</sub> /a1 (No. 14)	4	a = 15.1725 b = 5.6283 c = 3.7110 $\beta = 104.631^{\circ}$	<ul> <li>K: (0.16533, 0.02177, 0.29533)</li> <li>C: (0.11967,0.5150, -0.14363)</li> <li>O: (0.13329, 0.52915, 0.09482)</li> <li>(0.03221, 0.31998, -0.27353)</li> <li>(0.0761, 0.72772, -0.27448)</li> <li>H: (0.011, 0.6827, -0.465)</li> </ul>	a = 15.45481 (1.86) b = 5.71536 (1.52) c = 3.76864 (1.55) $\beta = 105.878^{\circ} (1.19)$	<ul> <li>K. (0.16530, 0.02299, 0.28726)</li> <li>C. (0.11977, 0.51149, -0.15485)</li> <li>O. (0.19443, 0.52683, 0.08663)</li> <li>(0.01246, 0.31928, -0.28688)</li> <li>(0.07793, 0.71698, -0.28240)</li> <li>H. (0.01434, 0.68811, -0.45755)</li> </ul>
K <sub>2</sub> CO <sup>3</sup>	P12 <sub>1</sub> /c1 (No. 14)	4	a = 5.63961 b = 9.8312 c = 6.83407 $\beta = 98.703^{\circ}$	K: (0.2418, 0.0831, 0.2148) (0.7391, 0.2602, 0.9720) C: (0.2455, 0.4174, 0.2489) O: (0.7588, 0.0430, 0.2014) (0.0631, 0.3488, 0.2770) (0.4147, 0.3609, 0.1718)	a = 5.76055 (2.14) b = 9.90478 (0.75) c = 7.18110 (5.08) $\beta = 97.295^{\circ} (-1.42)$	K: (0.24109, 0.08186, 0.19586) (0.74091, 0.26717, 0.97455) C: (0.25038, 0.41609, 0.25502) O: (0.73769, 0.04267, 0.19452) (0.06328, 0.34645, 0.27685) (0.42479, 0.35953, 0.18659)
<sup>a</sup> Taken from ref (	38. <sup>b</sup> Taken froi	n refs	17 and 18.			

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Table	2.	Calculated	Bond	Lengths a	d Hydrogen-	Bonding	Geometry"
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R(C-O1)	R(C-O2)	<i>R</i> (C–O3)	∠(O1-C-O2)	∠(01-C-O3)	∠(O2-C-O3)		
$1.289 (1.266^b)$	$1.310 \ (1.288^b)$	$1.312 (1.296^b)$	$120.5 (120.5^b)$	119.4 $(119.7^b)$	$120.1 \ (119.8^b)$		
$O_w$ — $H$ ···O'	$R(O_w-H)$	R(H…C	)')	$R(O_w \cdots O')$	$\angle(O_w - H \cdots O')$		
O4—H4A…O3	$1.008 (0.77^{c})$	1.658 (1.9	93 <sup>c</sup> )	$2.652 (2.686^c)$	167.90		
O5—H5A…O2	$1.00 (0.83^{c})$	1.719 (1.9	$90^{c}$ )	$2.713 (2.7135^{c})$	171.97		
O5—H5B…O3	$1.001 \ (0.69^c)$	1.662 (2.0	$03^{c})$	$2.659 (2.6709^{c})$	173.27		
<sup>a</sup> Bond lengths are in angstroms (Å) and bond angles are in degrees. <sup>b</sup> Taken from ref 51. <sup>c</sup> Taken from ref 52.							



Figure 2. Calculated electronic band structure of  $K_2CO_3$ ·1.5H<sub>2</sub>O. The Fermi level is set as relative zero.

the s and p orbitals of C and O. From Figure 3, it can be seen that the O of  $H_2O$  (denoted as  $O_w$  in Figure 1 and Tables 1 and 2) is different from the O of  $CO_3^{2-}$ : the s orbital of  $O_w$  interacting with s and p orbitals of H forms the band  $VB_7$  in Figure 2 with lowest energy, while its p orbitals interact with orbitals of H, C, and O to form other valence bands ( $VB_2-VB_4$ ). The s orbital of H also interacts with the p orbitals of O of  $CO_3^{2-}$  to form hydrogen bonds.

**III.B. Dynamic Phonon Properties.** As shown in Table 1, for  $K_2CO_3 \cdot 1.5H_2O$  there are eight formula units (f.u.) in its unit cell, but its primitive cell has only 4 f.u. with a total of 42 atoms. Therefore, there are 126 phonon modes in  $K_2CO_3 \cdot 1.5H_2O$ . The calculated phonon dispersion of  $K_2CO_3 \cdot 1.5H_2O$  is shown in Figure 4a. Along the wave vector L–A there is one soft mode that corresponds to the displacements of one type of O in  $CO_3^{2-}$ .

The calculated phonon densities of states of  $K_2CO_3 \cdot 1.5H_2O$ ,  $K_2CO_3$ ,<sup>38</sup> and  $KHCO_3$ <sup>18</sup> are shown in Figure 4b. Compared to anhydrous  $K_2CO_3$ ,  $K_2CO_3 \cdot 1.5H_2O$  has several extra peaks which corresponds to H (88–95 THz) and O (45–55 THz) of  $H_2O$ -related vibrations. In KHCO<sub>3</sub>, the HCO<sub>3</sub><sup>-</sup> moieties form



**Figure 3.** Calculated total density of states (TDOS) and projected partial density of states (PDOS) of  $K_2CO_3 \cdot 1.5H_2O$ . For comparison, the TDOS of  $K_2CO_3$  (No. 14)<sup>17,38</sup> is also plotted in the TDOS figure.

hydrogen-bound dimers  $(HCO_3^-)_2$  which are separated by K<sup>+</sup> ions.<sup>18</sup> As shown in Figure 1, for K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O, through the hydrogen bonding, CO<sub>3</sub><sup>2-</sup> anions are linked into the chain structure with a H<sub>2</sub>O linker. Obviously, from Figure 4b, the hydrogen bonding in K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O is weaker than that in

Table 3. DFT Calculated Energies  $(E_{DFT})$ , Band Gap, Zero-Point Energy  $(E_{ZP})$ , and Entropy (S) Calculated from Phonon and Available Experimental Data

					S (J/1	nol·K)
compound	space group	$E_{\rm DFT}$ (eV/f.u.)	band gap (eV)	$E_{\rm ZP}$ (eV/f.u.)	phonon $(T = 300 \text{ K})$	$expt^{a}$ (T = 298.15 K)
$K_2CO_3 \cdot 1.5H_2O$	C12/c1 (No. 15)	-59.494 83	4.298 (direct)	1.492 22	217.386	
КНСО <sub>3</sub> <sup>ь</sup>	P12 <sub>1</sub> /a1 (No. 14)	-37.886 04	4.967 (direct)	0.760 68	122.406	115.499
$K_2CO_3^c$	<i>P</i> 12 <sub>1</sub> / <i>c</i> 1 (No. 14)	-36.904 80	3.697 (direct)	0.457 33	160.121	155.500
CO <sub>2</sub> molecule	P1	-22.994 09		0.315 98		213.388
H <sub>2</sub> O molecule	P1	-14.272 67		0.558 41		188.832
	26	1				

<sup>*a*</sup>Taken from HSC Chemistry Package.<sup>36</sup> <sup>*b*</sup>Taken from refs 18 and 38. <sup>*c*</sup>Taken from refs 17 and 38.



**Figure 4.** Calculated phonon dispersions and phonon total density of states (PTDOS) of  $K_2CO_3$ ·1.5H<sub>2</sub>O. For comparison, the corresponding PTDOS of  $K_2CO_3$  and KHCO<sub>3</sub> are also plotted.

 $KHCO_3$  because the latter has lower frequency of H vibration (peak within 75–85 THz).

The calculated phonon free energy of K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O versus temperature is shown in Figure 5a, from which the zero-point energies  $(E_{ZP})$  can be obtained and are listed in Table 3. In order to compare their properties for capturing CO2, the thermodynamic properties of anhydrous K<sub>2</sub>CO<sub>3</sub> and KHCO<sub>3</sub> are also shown in Figure 5. The zero-point energies of these solids are significant and must be included in predicting their thermodynamic properties (eq 2). With increasing temperature, the free energy of K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O decreases faster than those of anhydrous K<sub>2</sub>CO<sub>3</sub> and KHCO<sub>3</sub>. Figure 5b shows the calculated entropies of these solids versus the temperature. Obviously, at 0 K, their entropies are zero and increase with increasing temperature. Because the structure of K2CO3·1.5H2O has a larger configuration entropy than K<sub>2</sub>CO<sub>3</sub> and KHCO<sub>3</sub>, its entropy is higher over the temperature range. Our previous results on other solids indicated that with our approach the calculated entropy of solids is quite close to the experimentally measured values.<sup>16,17,39</sup> Although in the literature there are no experimental data available for K2CO3.1.5H2O, our calculated entropy should be consistent with the experimentally measured value. By including these free energies and entropies at different temperatures in eqs 1-3, the thermodynamic properties of the reactions of K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O and anhydrous K<sub>2</sub>CO<sub>3</sub> capturing CO<sub>2</sub> can be evaluated as described in section III.C.



**Figure 5.** Calculated phonon free energy and entropy of  $K_2CO_3$ ·1.5H<sub>2</sub>O. For comparison, the corresponding data of  $K_2CO_3$  and KHCO<sub>3</sub> are also plotted.

III.C. Capabilities of K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O To Capture CO<sub>2</sub>. According to eq 3, the calculated heats of reaction (enthalpy change) for reactions R1 and R2 versus temperature are plotted in Figure 6a. Obviously, along the temperature range, the anhydrous K<sub>2</sub>CO<sub>3</sub> capture of CO<sub>2</sub> can release more reaction heat than the hydrated K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O. This means the interaction of  $\mathrm{K}_2\mathrm{CO}_3$  with  $\mathrm{CO}_2$  is much stronger than that of  $K_2CO_3 \cdot 1.5H_2O$ , and during the regeneration stage, more energy is required to regenerate  $K_2CO_3$ . With  $P_{eas} = 1$  bar, Figure 6b shows the calculated Gibbs free energy of these two reactions versus temperature. The slope of the free energy versus temperature for the reaction  $K_2CO_3 + H_2O(g) + CO_2 =$  $2KHCO_3$  is larger than that of  $K_2CO_3 \cdot 1.5H_2O + CO_2 =$ 2KHCO<sub>3</sub> + 0.5H<sub>2</sub>O(g). This indicates that the driving force for  $K_2CO_3$  to capture a  $CO_2$  is larger than that of  $K_2CO_3 \cdot 1.5H_2O_2$ , and the energy needed to reverse the  $\Delta G > 0$  for reaction R2 is larger than that for the forward reaction.

By examining eq 1, for the reaction of  $K_2CO_3$ ·1.5H<sub>2</sub>O capturing CO<sub>2</sub>, we can explore the relationship among the chemical potential ( $\Delta\mu(T,P)$ ), temperature, and CO<sub>2</sub> pressure ( $P_{CO_2}$ ) at several fixed values of  $P_{H_2O}$ . This kind of relationship for reactions R1 and R2 is shown in Figure 7 as a contour plot in a two-dimensional representation. The lines in Figure 7



**Figure 6.** Calculated thermodynamic properties of  $K_2CO_3 \cdot 1.5H_2O$  and  $K_2CO_3$  reacting with  $CO_2$ . (a) Heat of reaction versus temperature; (b) Gibbs free energy versus temperature.

indicate conditions at which  $\Delta\mu(T,P) = 0$ . Near these lines is a good region for energy-efficient absorption and desorption because of the minimal energy costs at the given temperature and pressure. Above these lines in Figure 7 ( $\Delta\mu(T,P) < 0$ ), the solids K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O and K<sub>2</sub>CO<sub>3</sub> are respectively favored to absorb CO<sub>2</sub> and to form KHCO<sub>3</sub>, while below these lines ( $\Delta\mu(T,P) < 0$ ) KHCO<sub>3</sub> is favored to release CO<sub>2</sub>, regenerating the solid sorbent.

From Figure 7 one can see that at each fixed  $P_{H_2O}$  these two lines of the reactions for  $K_2CO_3 \cdot 1.5H_2O$  and  $K_2CO_3 \cdot 1.5H_2O$ capturing  $CO_2$  cross at a transition temperature  $(T_{tr})$ , which means that at this temperature there is a phase transition  $K_2CO_3 \cdot 1.5H_2O \leftrightarrow K_2CO_3 + 1.5H_2O$  happening. Obviously, at each fixed  $P_{H_2O}$ , the  $T_{tr}$  is fixed and does not depend on  $P_{CO_2}$  as shown with vertical lines in Figure 7. Therefore, in Figure 7 the phase diagram has three regions corresponding to three solid phases: the region below  $T_{tr}$  and under the line is  $K_2CO_3 \cdot 1.5H_2O$ , the region above  $T_{tr}$  and under the line is  $K_2CO_3$ , while the rest of the region above the lines is the KHCO<sub>3</sub> phase. In other words, below  $T_{tr}$  only reaction R1 can happen and only  $K_2CO_3 \cdot 1.5H_2O$  could be regenerated, while above  $T_{tr}$  reaction R2 can happen and anhydrous  $K_2CO_3$  could be regenerated.



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**Figure 7.** Contour plots of calculated chemical potentials ( $\Delta\mu$ ) versus temperatures and CO<sub>2</sub> pressures at several fixed H<sub>2</sub>O pressures and temperatures for K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O and K<sub>2</sub>CO<sub>3</sub><sup>17,18,38</sup> capturing CO<sub>2</sub>. The *y*-axis is given in logarithmic scale. Only  $\Delta\mu = 0$  curves with different fixed P<sub>H<sub>2</sub>O</sub> values are shown explicitly. For each reaction, above the  $\Delta\mu = 0$  curve, the carbonates absorb CO<sub>2</sub> and the reaction goes forward ( $\Delta\mu < 0$  region) to form bicarbonate, whereas below the  $\Delta\mu = 0$  curve, the bicarbonate releases CO<sub>2</sub> and the reaction goes backward to regenerate the carbonates ( $\Delta\mu > 0$  region).

As shown in Figure 7 and eq 1,  $\Delta \mu(T,P)$  is dependent not only on temperature but also on gas pressure ( $P_{\text{gas}}$ ). For reaction R1  $P_{\text{gas}} = P_{\text{CO}_2} / (P_{\text{H}_2\text{O}}P_0)^{1/2}$ , while for reaction R2  $P_{\text{gas}} = P_{\text{CO}_2}P_{\text{H}_2\text{O}}/P_0^2$ , where  $P_0 = 1$  bar is the reference pressure. Even with the same  $P_{\text{CO}_2}$ ,  $P_{\text{H}_2\text{O}}$  plays a different role in reactions R1 and R2. The behavior can be discussed in more detail by setting  $P_{\text{H}_2\text{O}}$  at several values giving different scenarios as shown in Figure 7.

(i) The first scenario is  $P_{H_2O} = 1.0$  bar, which corresponds to the saturation pressure of water vapor at 100 °C. In this case, the  $P_{gas}$  values for reactions R1 and R2 are the same and equal  $P_{CO_2}$ . From Figure 7, these two lines cross at  $T_{tr1} = 445$  K (172 °C), which means above this temperature ( $T_{tr1}$ ) the hydrated  $K_2CO_3 \cdot 1.5H_2O$  will be dehydrated to  $K_2CO_3$  through the phase transition reaction of  $K_2CO_3 \cdot 1.5H_2O \leftrightarrow K_2CO_3 + 1.5H_2O$ , which agrees with the experimental findings that hydrates of  $K_2CO_3 \cdot 1.5H_2O$  can be stable up to 153 °C at ambient atmosphere condition.<sup>51</sup> As one can see from Figure 7, both of these reactions are thermodynamically favorable over a wide range of temperature and  $P_{CO_2}$ , which means that under this temperature range the absorption of  $CO_2$  is thermodynamically favored by  $K_2CO_3$  and  $K_2CO_3 \cdot 1.5H_2O$ .

However, as a  $CO_2$  solid sorbent, it should not only be easy to absorb  $CO_2$  in the capture cycle but also be easy to release the  $CO_2$  during the regeneration cycle. The operating conditions for absorption/desorption processes depend on their use in a pre- or a postcombustion application. The U.S. Department of Energy (DOE) programmatic goal for postcombustion and oxy-combustion  $CO_2$  capture is to capture at least 90% of the  $CO_2$  produced by a plant with the cost in electricity increasing no more than 35%, whereas the goal in the case of precombustion  $CO_2$  capture is to capture at least 90% of the  $CO_2$  produced with the cost in electricity increasing no more than 10%.<sup>54–56</sup> Under precombustion conditions, after the water gas shift reactor, the gas stream mainly contains  $CO_2$ ,  $H_2O$ , and  $H_2$ . The partial  $CO_2$  pressure could be as high as 20– Table 4. Calculated Thermodynamic Properties of Reactions of CO<sub>2</sub> Captured by Hydrated and Dehydrated Potassium Carbonates (in kJ/mol); Highest Temperature for Carbonates Capturing CO<sub>2</sub> at Precombustion ( $T_1$ ) ( $P_{CO_2} = 20$  bar) and Postcombustion ( $T_2$ ) ( $P_{CO_2} = 0.1$  bar) Conditions and Phase Transition Temperature ( $T_{tr}$ ) of K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O into K<sub>2</sub>CO<sub>3</sub>

reaction	CO <sub>2</sub> (wt %)	$\Delta E_{ m DFT}$	$\Delta E_{ m ZP}$	$\Delta H(T = 300 \text{ K})$	$\Delta G(T = 300 \text{ K})$	$T_1$ (K)	$T_2$ (K)	$T_{\rm tr}$ (K)		
$K_2CO_3 \cdot 1.5H_2O + CO_2 = 2KHCO_3 + 0.5H_2O(g)$	26.88	-40.474	-0.737	-40.678	-12.820	580 <sup>b</sup>	370 <sup>b</sup>	445 <sup>b</sup>		
						665 <sup>c</sup>	395 <sup>c</sup>	395 <sup>c</sup>		
						510 <sup>d</sup>	335 <sup>d</sup>	515 <sup>d</sup>		
$K_2CO_3 + CO_2 + H_2O(g) = 2KHCO_3$	31.84	-154.429	18.293	-141.728	-46.281	490 <sup>b</sup>	420 <sup>b</sup>			
				$-142.854^{a}$	$-44.716^{a}$	455 <sup>c</sup>	395 <sup>c</sup>			
						515 <sup>d</sup>	445 <sup>d</sup>			
<sup>a</sup> Calculated by HSC Chemistry package. <sup>36</sup> <sup>b</sup> When $P_{H,O} = 1$ bar. <sup>c</sup> When $P_{H,O} = 0.1$ bar. <sup>d</sup> When $P_{H,O} = 10$ bar.										

30 bar, and the temperature is around 313-573 K. To minimize the energy consumption, the ideal sorbents should work in these pressure and temperature ranges to separate CO<sub>2</sub> from  $H_2$ . The temperature denoted  $T_1$  and listed in Table 4 is the temperature above which the sorbent solids cannot absorb CO<sub>2</sub> and will start to release CO<sub>2</sub>. This indicates that, during the capture cycle, the operating temperature should be lower than  $T_1$ , whereas the temperature may be higher than  $T_1$ (depending on the desired  $CO_2$  pressure) during the regeneration cycle. Under postcombustion conditions, the gas stream mainly contains CO<sub>2</sub> and N<sub>2</sub>, the partial pressure of  $CO_2$  is in the range 0.1–0.2 bar, and the temperature range  $(T_2)$  is quite different. Currently, in postcombustion CO<sub>2</sub> capture technology, the amine-based solvents and carbonand zeolite-based solid sorbents (including metal organic framework) capture  $CO_2$  within a lower temperature range (<200 °C),<sup>4</sup> while oxides (CaO, Na<sub>2</sub>O, etc.) and salts (Li<sub>4</sub>SiO<sub>4</sub>, Li<sub>2</sub>ZrO<sub>3</sub>, etc.) capture CO<sub>2</sub> usually within a higher temperature range (>400 °C).<sup>4,16,17,39–41</sup>

The turnover temperatures (denoted as  $T_1$  and  $T_2$ ) for preand postcombustion capture by K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O and K<sub>2</sub>CO<sub>3</sub>, as well as their phase transition temperatures  $(T_{tr})$ , are listed in Table 4. For  $K_2CO_3$ ·1.5H<sub>2</sub>O,  $T_1$  and  $T_2$  are 580 and 370 K, respectively. As discussed above and shown in Figure 6,  $K_2CO_3 \cdot 1.5H_2O$  can only be stable below  $T_{tr1} = 445$  K. Since its  $T_1 > T_{trl}, K_2 CO_3 \cdot 1.5 H_2 O$  cannot be used for precombustion  $CO_2$  capture technology, but can be applied to postcombustion  $CO_2$  capture technology because its  $T_2 < T_{tr1}$ . As shown in Figure 7, K<sub>2</sub>CO<sub>3</sub> could be used for both post- and precombustion CO<sub>2</sub> capture technologies. However, if the operating temperature for the regeneration step is lower than  $T_{tr1}$ , KHCO<sub>3</sub> will be first regenerated into K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O, not  $K_2CO_3$ . When the operating temperature is higher than  $T_{tr1}$ , KHCO<sub>3</sub> will be first regenerated into K<sub>2</sub>CO<sub>3</sub>, not K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O, regardless of whether the initial solid sorbent is K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O or K<sub>2</sub>CO<sub>3</sub>.

(ii) The second scenario for showing the role of  $P_{\rm H_2O}$  in reactions R1 and R2 is when  $P_{\rm H_2O} < 1.0$  bar, which corresponds to the saturation pressure of water vapor below 100 °C. Here we only discuss one example with  $P_{\rm H_2O} = 0.1$  bar, which corresponds to the saturation pressure of water vapor at around 47 °C. In this case, the gas pressure  $(P_{\rm gas})$  is different for reactions R1 and R2:  $P_{\rm gas}^{\rm R1} = P_{\rm CO_2}^{\rm R1}/(P_{\rm H_2O}P_0)^{1/2}$  and  $P_{\rm gas}^{\rm R2} = P_{\rm CO_2}^{\rm R2}P_{\rm H_2O}/P_0^2$ . From this one can see that, with decreasing  $P_{\rm H_2O}$ ,  $P_{\rm CO_2}^{\rm R1} < P_{\rm CO_2}^{\rm R2}$  under the same  $P_{\rm gas}$ . Therefore, compared with case i, with black lines in Figure 7, in this case (red lines) the  $\Delta\mu = 0$  curve of reaction R1 for K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O capturing CO<sub>2</sub> shifted

down while the  $\Delta \mu = 0$  curve of reaction R2 for K<sub>2</sub>CO<sub>3</sub> capturing CO<sub>2</sub> moved up. Hence, it can be expected that the phase transition temperature  $(T_{tr2})$  of  $K_2CO_3 \cdot 1.5H_2O$  into  $K_2CO_3$  could be lower when  $P_{H_2O}$  is decreased. Indeed, from Figure 7, the calculated  $T_{tr2}$  is 395 K, which is lower than  $T_{tr1}$  = 445 K. At  $T_{\rm tr2}$  = 395 K, the corresponding CO<sub>2</sub> pressure is about 0.1 bar, which matches the postcombustion CO<sub>2</sub> pressure condition. Therefore, although it is not suitable for precombustion CO<sub>2</sub> capture since its  $T_1 = 665$  K >  $T_{tr2} =$ 395 K, compared to case i,  $K_2CO_3 \cdot 1.5H_2O$  may still be used for postcombustion CO<sub>2</sub> capture technology with lower operating temperature ( $\leq$ 395 K, when  $P_{H_2O} \leq 0.1$  bar) as its  $T_2 = 395$  K  $\approx$  T<sub>tr2</sub>. By increasing P<sub>H2O</sub> from 0.1 to 1 bar (Figure 7), T<sub>tr2</sub> could reach  $T_{trl}$ . Again, similar to case i shown in Figure 7, if the regeneration operating temperature is higher than  $T_{tr2}$  only anhydrous K<sub>2</sub>CO<sub>3</sub> can be obtained. As shown in Table 4, the corresponding T1 and T2 for K2CO3 are 455 and 395 K, respectively. This means that under this steam pressure K<sub>2</sub>CO<sub>3</sub> is only suitable for precombustion  $CO_2$  capture while  $K_2CO_3 \cdot 1.5H_2O$  could be used for postcombustion  $CO_2$  capture technology. If one expects to regenerate  $K_2CO_3$ ·1.5H<sub>2</sub>O, the operating regeneration temperature must be lower than  $T_{tr2}$ . In other words, case ii serves as the low end for the steam pressure, which means that, in order to use K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O as  $CO_2$  sorbent, the steam pressure should be higher than 0.1 bar.

(iii) The last scenario is when  $P_{\rm H,O}$  > 1.0 bar, which corresponds to the saturation pressure of water vapor above 100 °C. Here we also discuss one example of  $P_{\rm H,O}$  = 10 bar. In this case,  $P_{\text{gas}}$  is also different for reactions R1 and R2:  $P_{\text{gas}}^{\text{R1}} = P_{\text{CO}_2}/(P_{\text{H}_2\text{O}}P_0)^{1/2}$  and  $P_{\text{gas}}^{\text{R2}} = P_{\text{CO}_2}P_{\text{H}_2\text{O}}/P_0^{-2}$ . With increasing  $P_{\rm H_2O_2}$ ,  $P_{\rm CO_2}^{\rm R1}$  is greater than  $P_{\rm CO_2}^{\rm R2}$  under the same  $P_{\rm gas}$ . Compared with cases i and ii, it can be expected that the phase transition temperature of K2CO3·1.5H2O into K2CO3 could be higher when  $P_{\rm H,O}$  was increased, because the  $\Delta \mu = 0$  curve of reaction R1 for K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O capturing CO<sub>2</sub> moved up while the  $\Delta \mu$ = 0 curve of reaction R2 for  $K_2CO_3$  capturing  $CO_2$  shifted down as shown by the green lines in Figure 7. Indeed,  $T_{tr3}$  = 515 K is greater than  $T_{tr1}$  = 445 K. Compared to case i, when  $K_2CO_3 \cdot 1.5H_2O$  is used for postcombustion  $CO_2$  capture technology, its highest absorption temperature is around  $T_2$  = 335 K and its regenerating temperature range is 335-515 K. Above  $T_{tr3}$  = 515 K, the regenerated solid is anhydrous K<sub>2</sub>CO<sub>3</sub>, not K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O. When K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O is used as sorbent for precombustion CO<sub>2</sub> capture technology, its highest absorption temperature is around  $T_1 = 510$  K and its regenerating temperature range is very narrow with 510-515 K if we want to obtain a high pressure of CO<sub>2</sub> ( $\approx$ 20 bar as before the capture). Above  $T_{tr3} = 515$  K, instead of regenerating  $K_2CO_3$ ·1.5H<sub>2</sub>O, anhydrous  $K_2CO_3$  will be obtained. Below  $T_{tr3}$ = 515 K, regenerating  $K_2CO_3$ ·1.5H<sub>2</sub>O is possible, but with low released CO<sub>2</sub> pressure. In conclusion, at high steam pressure (at least >1.0 bar),  $K_2CO_3$ ·1.5H<sub>2</sub>O could be used as CO<sub>2</sub> sorbent for both post- and precombustion CO<sub>2</sub> capture technologies.

Overall, from Figure 7 one can see that decreasing  $P_{\rm H_2O}$  will enhance the ability of  $K_2\rm CO_3 \cdot 1.5\rm H_2O$  to capture  $\rm CO_2$  and move its turnover temperature higher because, as shown in reaction R1, H<sub>2</sub>O is on the product side. For the case of anhydrous  $K_2\rm CO_3$ , decreasing  $P_{\rm H_2O}$  will weaken its capacity for  $\rm CO_2$  capture and move its turnover temperature lower as listed in Table 4 because, as shown in reaction R2, H<sub>2</sub>O is on the reactant side. The phase transition temperature of  $K_2\rm CO_3 \cdot 1.5\rm H_2O$  into  $K_2\rm CO_3$  increases with increase of the steam pressure  $P_{\rm H_2O}$ . In order to use  $K_2\rm CO_3 \cdot 1.5\rm H_2O$  as an efficient  $\rm CO_2$  sorbent in postcombustion capture technology, the best steam pressure range should be less than 1.0 bar, while in precombustion  $\rm CO_2$  capture technology, the best steam pressure range should be greater than 1.0 bar.

# **IV. CONCLUSIONS**

By combining density functional theory and phonon lattice dynamics, the electronic structural and phonon properties of  $K_2CO_3$ ·1.5H<sub>2</sub>O were investigated. The optimized structure of this solid is in good agreement with experimental measurements.  $K_2CO_3$ ·1.5H<sub>2</sub>O has a direct band gap of 4.298 eV. Similar to  $K_2CO_3$ , the p orbital of K forms a single valence band. Different from the O of  $CO_3^{2-}$ , the s orbital of O<sub>w</sub> in H<sub>2</sub>O interacts with s and p orbitals of H to form a band with the lowest energy, while its p orbitals interact with orbitals of H, C, and O to form other valence bands. The hydrogen bond in  $K_2CO_3$ ·1.5H<sub>2</sub>O is formed by interacting the s orbital of H with p orbitals of O of  $CO_3^{2-}$ .

The phonon dispersions and phonon density of states for  $K_2CO_3$ ·1.5H<sub>2</sub>O were calculated by the direct method. Among its 126 phonon modes, one soft mode along the wave vector L–A was found and corresponded to one type of O displacement.

From the calculated thermodynamic properties of  $K_2CO_3 \cdot 1.5H_2O$  and  $K_2CO_3$  reacting with  $CO_2$  through reactions  $K_2CO_3 \cdot 1.5H_2O + CO_2 = 2KHCO_3 + 0.5H_2O(g)$  and  $K_2CO_3 + H_2O(g) + CO_2 = 2KHCO_3$ , it was found that the  $K_2CO_3 \cdot 1.5H_2O$  is better applied for postcombustion  $CO_2$  capture technology at a temperature lower than its phase transition temperature which depends on the  $CO_2$  pressure and the steam pressure ( $P_{H_2O} \le 1.0$  bar). When  $P_{H_2O} > 1.0$  bar, it is possible to use  $K_2CO_3 \cdot 1.5H_2O$  sorbent for precombustion  $CO_2$  capture. Above the phase transition temperature, the sorbent will be regenerated into anhydrous  $K_2CO_3$ . Compared to  $K_2CO_3$ ,  $K_2CO_3 \cdot 1.5H_2O$  requires less energy for regeneration.

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#### Notes

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#### REFERENCES

(1) Aaron, D.; Tsouris, C. Sep. Sci. Technol. 2005, 40, 321.

(2) White, C. M.; Strazisar, B. R.; Granite, E. J.; Hoffman, J. S.; Pennline, H. W. J. Air Waste Manage. Assoc. 2003, 53, 645.

(4) Wang, Q.; Luo, J.; Zhong, Z.; Borgna, A. Energy Environ. Sci. 2011, 4, 42.

(5) Wang, S. P.; Yan, S. L.; Ma, X. B.; Gong, J. L. Energy Environ. Sci. 2011, 4, 3805.

(6) Pennline, H. W.; Luebke, D. R.; Jones, K. L.; Myers, C. R.; Morsi,

- B. I.; Heintz, Y. J.; Ilconich, J. B. Fuel Process. Technol. 2008, 89, 897.
- (7) Ochoa-Fernandez, E.; Rusten, H. K.; Jakobsen, H. A.; Ronning, M.; Holmen, A.; Chen, D. *Catal. Today* **2005**, *106*, 41.
- (8) Haszeldine, R. S. Science 2009, 325, 1647.
- (9) Allen, M. R.; Frame, D. J.; Huntingford, C.; Jones, C. D.; Lowe, J. A.; Meinshausen, M.; Meinshausen, N. *Nature* **2009**, *458*, 1163.
- (10) Hoffman, J. S.; Pennline, H. W. Investigation of  $CO_2$  Capture Using Regenerable Sorbents. In *Proceedings of the 17th Annual International Pittsburgh Coal Conference*, Pittsburgh, PA, 2000; p P3\_7.
- (11) Lee, S. C.; Chae, H. J.; Lee, S. J.; Choi, B. Y.; Yi, C. K.; Lee, J. B.; Ryu, C. K.; Kim, J. C. *Environ. Sci. Technol.* **2008**, *42*, 2736.

(12) Lee, S. C.; Choi, B. Y.; Lee, S. J.; Jung, S. Y.; Ryu, C. K.; Kim, J. C. Stud. Surf. Sci. Catal. **2004**, 153, 527.

- (13) Lee, S. C.; Choi, B. Y.; Lee, T. J.; Ryu, C. K.; Soo, Y. S.; Kim, J. C. Catal. Today **2006**, 111, 385.
- (14) Lee, S. C.; Kim, J. C. Catal. Surv. Asia 2007, 11, 171.
- (15) Lee, S. C.; Chae, H. J.; Lee, S. J.; Park, Y. H.; Ryu, C. K.; Yi, C.
- K.; Kim, J. C. J. Mol. Catal. B: Enzym. 2009, 56, 179.
- (16) Duan, Y.; Sorescu, D. C. J. Chem. Phys. 2010, 133, 074508.
- (17) Duan, Y.; Zhang, B.; Sorescu, D. C.; Johnson, J. K. J. Solid State Chem. 2011, 184, 304.
- (18) Duan, Y.; Zhang, B.; Sorescu, D. C.; Johnson, J. K.; Majzoub, E. H.; Luebke, D. Density functional theory studies on the electronic, structural, phonon dynamical and thermo-stability properties of bicarbonates  $MHCO_3$ , M = Li, Na, K. J. Phys.: Condens. Matter 2012.
- (19) Dutcher, B.; Fan, M.; Leonard, B.; Dyar, M. D.; Tang, J.;
  Speicher, E. A.; Liu, P.; Zhang, Y. J. Phys. Chem. C 2011, 115, 15532.
  (20) Dutcher, B.; Fan, M. H.; Leonard, B. Sep. Purif. Technol. 2011, 80, 364.
- (21) Liang, Y.; Harrison, D. P.; Gupta, R. P.; Green, D. A.; McMichael, W. J. Energy Fuels 2004, 18, 569.
- (22) Zhao, C. W.; Chen, X. P.; Zhao, C. S.; Liu, Y. K. Energy Fuels 2009, 23, 1766.
- (23) Lee, J. B.; Ryu, C. K.; Baek, J. I.; Lee, J. H.; Eom, T. H.; Kim, S. H. Ind. Eng. Chem. Res. 2008, 47, 4465.
- (24) Park, Y. C.; Jo, S. H.; Ryu, C. K.; Yi, C. K. Energy Procedia 2009, 1, 1235.
- (25) Shigemoto, N.; Yanagihara, T.; Sugiyama, S.; Hayashi, H. Energy Fuels 2006, 20, 721.
- (26) Chi, Z. Y.; O'Fallon, J. V.; Chen, S. L. Trends Biotechnol. 2011, 29, 537.
- (27) Zhao, C. W.; Chen, X. P.; Zhao, C. S. Energy Fuels 2009, 23, 4683.
- (28) Zhao, C. W.; Chen, X. P.; Zhao, C. S. Int. J. Greenhouse Gas Control **2010**, *4*, 655.
- (29) Zhao, C. W.; Chen, X. P.; Zhao, C. S. Ind. Eng. Chem. Res. 2010, 49, 12212.
- (30) Zhao, C. W.; Chen, X. P.; Zhao, C. S. Ind. Eng. Chem. Res. 2011, 50, 4464.

(31) Lee, S. C.; Chae, H. J.; Kwon, Y. M.; Lee, W. S.; Nam, H. S.; Jung, S. Y.; Lee, J. B.; Ryu, C. K.; Kim, J. C. J. Nanoelectron. Optoelectron. 2010, 5, 212.

<sup>(3)</sup> Pires, J. C. M.; Martins, F. G.; Alvim-Ferraz, M. C. M.; Simoes, M. Chem. Eng. Res. Des. 2011, 89, 1446.

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- (32) Li, L.; Li, Y.; Wen, X.; Wang, F.; Zhao, N.; Xiao, F. K.; Wei, W.; Sun, Y. H. *Energy Fuels* **2011**, *25*, 3835.
- (33) Zhao, C. W.; Chen, X. P.; Zhao, C. S. Energy Fuels 2012, 26, 1401.
- (34) Hirano, S.; Shigemoto, N.; Yamada, S.; Hayashi, H. Bull. Chem. Soc. Jpn. 1995, 68, 1030.
- (35) Hayashi, H.; Taniuchi, J.; Furuyashiki, N.; Sugiyama, S.; Hirano, S.; Shigemoto, N.; Nonaka, T. *Ind. Eng. Chem. Res.* **1998**, *37*, 185.
- (36) HSC Chemistry software 6.1; Outotec Research Oy, Pori, Finland; www.outotec.com/hsc, 2006.
- (37) Chase, M. W. J. J. Phys. Chem. Ref. Data, Monogr. 1998, 9, 1.
- (38) Duan, Y. J. Renewable Sustainable Energy 2012, 4, 013109.
- (39) Duan, Y.; Parlinski, K. Phys. Rev. B 2011, 84, 104113.
- (40) Duan, Y.; Sorescu, D. C. Phys. Rev. B 2009, 79, 014301.
- (41) Duan, Y. J. Renewable Sustainable Energy 2011, 3, 013102.
- (42) Zhang, B.; Duan, Y.; Johnson, J. K. J. Chem. Phys. 2012, 136, 064516.
- (43) Kresse, G.; Hafner, J. Phys. Rev. B 1993, 47, 558.
- (44) Kresse, G.; Furthmuller, J. Phys. Rev. B 1996, 54, 11169.
- (45) Perdew, J. P.; Wang, Y. Phys. Rev. B 1992, 45, 13244.
- (46) Duan, Y. Phys. Rev. B 2008, 77, 045332.
- (47) Monkhorst, H. J.; Pack, J. D. Phys. Rev. B 1976, 13, 5188.
- (48) Bradley, C. J.; Cracknell, A. P. The Mathematical Theory of Symmetry in Solids; Clarendon Press: Oxford, U.K., 1972.
- (49) Parlinski, K. Software PHONON, 2010.
- (50) Parlinski, K.; Li, Z. Q.; Kawazoe, Y. Phys. Rev. Lett. 1997, 78, 4063.
- (51) Hunter, F. D.; Jeffrey, G. A. J. Chem. Phys. 1967, 47, 3297.
- (52) Skakle, J. M. S.; Wilson, M.; Feldmann, J. Acta Crystallogr., Sect. E 2001, 57, 194.
- (53) Ireta, J.; Neugebauer, J.; Scheffler, M. J. Phys. Chem. A 2004, 108, 5692.
- (54) DOE-NETL. Cost and Performance Baseline for Fossil Energy Plants, Vol. 1: Bituminous Coal and Natural Gas to Electricity Final Report; http://www.netl.doe.gov/energy-analyses/baseline\_studies. html, 2007.
- (55) Figueroa, J. D.; Fout, T.; Plasynski, S.; McIlvried, H.; Srivastava, R. D. Int. J. Greenhouse Gas Control **2008**, *2*, 9.
- (56) DOE/NETL. Carbon Dioxide Capture and Storage RD&D Roadmap; http://www.netl.doe.gov/technologies/carbon\_seq/ refshelf/CCSRoadmap.pdf, 2010.

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