Oxygen Scrambling of CO₂ Adsorbed on CaO(001)

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Supporting Information

ABSTRACT: The adsorption of CO_2 on CaO(001) is investigated by density functional theory and infrared reflection absorption spectroscopy (IRAS). The calculations show that isolated CO_2 adsorbates on terraces as monodentate carbonates can freely rotate at room temperature, while rotation within carbonate aggregates has some hindrance. Rotation and other motions are important to facilitate oxygen atom exchange between the CO_2 adsorbate and CaO lattice. The calculated intrinsic barrier to oxygen scrambling is 114 kJ/ mol for an isolated carbonate species and 148 kJ/mol within a long carbonate chain. However, due to the large adsorption energy for CO_2 on a defect-free CaO terrace site, the



apparent barrier becomes -39 kJ/mol for an isolated carbonate. At lower coordinated sites with higher degrees of freedom, the calculated intrinsic barrier to oxygen atom exchange is 80 kJ/mol at filled monatomic step sites and 26.9 kJ/mol at corner sites. IRAS studies are performed by adsorbing C¹⁸O₂ on well-ordered Ca¹⁶O films grown on Mo and Ru substrates. The magnitude and splitting of the red shifts due to isotopic labeling are rationalized when considering oxygen scrambling, such that observed normal modes of surface carbonates involve both ¹⁶O–C and ¹⁸O–C vibrations. As previously assigned, the earliest observable infrared peaks are due to adsorption at step sites, and additional observable peaks are due to aggregation of carbonates on terraces.

INTRODUCTION

Carbon dioxide (CO_2) is an abundant chemical feedstock with wide application in industry.^{1,2} Environmental concerns have driven much research into CO₂ interactions with alkaline-earth oxides, such as calcium oxide (CaO), which have utility for carbon capture and catalysis.³⁻⁵ For sequestration application, the capacity for CO₂ adsorption on CaO powders is dependent on particle size, where carbonation results in formation of outer calcium carbonate (CaCO₃) layers.^{6,7} Nucleation of CaCO₃ formation, which is related to the partial pressure of gaseous CO₂, occurs quickly, followed by slow growth of CaCO₃, which is diffusion-controlled.^{8,9} Modeling of this nucleation process was designed to gain insight into catalyst regeneration in the carbon sequestration effort.^{10,11} Electron spectroscopic techniques indicated $CaCO_3$ also forms a top layer upon CO_2 adsorption on CaO(001) thin films and single crystals.^{12,13} However, the thin films were characterized as polycrystalline, and the single crystal was contaminated with water in the ultrahigh vacuum (UHV) system. In a molecular beam experiment on a CaO(001) crystal, a preponderance of defects, assigned to oxygen vacancies, led to the decomposition of CO₂ to CO.¹⁴ Therefore, great interest is focused on the initial stages of CO₂ adsorption before CaCO₃ formation, especially on defect-free, monocrystalline CaO surfaces.

Formation of surface carbonate (CO_3^{2-}) species on CaO(001) powder has been proposed by an early infrared spectroscopy study,¹⁵ while numerous theoretical reports corroborated such an assignment on terrace, edge, step, and corner sites.^{16–20} Recently, we presented a joint experimental-theoretical investigation on CO₂ adsorption on CaO(001) in the low coverage regime.²¹ Thin films of CaO(001) were

grown on a Mo(001) substrate, which have been shown to be nearly defect-free and exhibit properties virtually identical to the bulk.²²⁻²⁴ Infrared reflection absorption spectroscopy (IRAS) experiments of CO₂ on CaO(001) showed vibrational modes consistent with surface carbonates. We assigned the bands in the IRA spectra as resulting from monodentate carbonate species that first adsorb at steps and other lowcoordinated sites, followed by surface islanding of monodentate carbonates adsorbed on terraces. The aggregation of adsorbates on terraces was consistent with previous computational results²⁵ and microcalorimetry experiments that observed a coverage effect of CO₂ adsorption.²¹ The adsorption of CO₂ onto metals and metal-oxide surfaces has been probed by experimental techniques to compare the properties of different surfaces and to study the effects of morphology and surface defects.²⁶⁻³⁰

Temperature-programmed CO₂ desorption experiments on MgO and CaO utilized isotopically labeled $C^{18}O_2$.^{31–33} Both $C^{16}O_2$ and mixed $C^{16}O^{18}O$ were observed upon desorption at room temperature, indicating that oxygen atoms of the adsorbate can exchange with the oxide surface lattice. Single and double oxygen atom exchange were explained by formation of bidentate carbonate that can either migrate along the surface before dissociation upon heating, or react with nearby oxygen vacancies that are readily available at low-coordinated sites. Small cluster calculations were used to verify the plausibility of an oxygen scrambling mechanism of CO₂ on MgO via low-

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coordinated sites and nearby oxygen vacancies.^{31,32} To the best of our knowledge, no computational study of lattice oxygen exchange of CaO with CO_2 exists in the literature.

Oxygen atom exchange has been demonstrated on alkalineearth oxides from other adsorbates. The reactivity of aldehydes, resulting in dimerized ether products via the Tishchenko reaction, was found to have surface oxygen atom exchange. It was similarly concluded that the oxygen atom exchange mechanism required bidentate structures involving oxygen vacancies or coordinative unsaturated sites.^{34,35} Oxygen atom exchange from molecular oxygen on MgO, CaO, and SrO surfaces has also been demonstrated experimentally.³⁶ Based on a computational analysis, coordinative unsaturated sites are employed within the mechanism to ensure oxygen atom exchange.³⁷

In this study, we provide further evidence for the assignment of the observed IRAS bands²¹ by dosing C¹⁸O₂ on a Ca¹⁶O film grown on Mo(001) and Ru(0001) substrates. We use density functional theory (DFT) to show that the observed shifts on isotope exchange can be rationalized within the framework of the previous peak assignments. We calculate the vibrational frequencies for oxygen isotope exchange with the Ca¹⁶O lattice for different exchange patterns. To determine the likelihood of various exchange processes, we calculate reaction energies and energy barriers for CO₂ adsorbed on different morphological sites of the CaO(001) surface such as terraces, steps, and corners, which have been proposed to be active for oxygen scrambling of CO₂ adsorption on rock salt oxides.^{31,32} We do this both for isolated species and for species within aggregates. We do not consider other types of defects such as oxygen vacancies in this study which, on adsorption of CO₂, would be healed and yield CO.

MODELS AND METHODS

Models. The CaO(001) surface was modeled with neutral clusters and periodic slabs from our previous study,²¹ described in Table 1. The cluster models are composed of Ca and O atoms that can relax structurally, as well as additional Ca atoms that are represented by all-electron effective core potentials (ECPs).³⁸ The clusters are embedded in a 2D-periodic field of point charges extending six layers deep, where the outermost

Table 1. Cluster and Periodic Models Used in This Study

morphology	model	type	composition ^a
terrace	T1	cluster	${Ca_5O_{14}Ca_{9}^{fix}Ca_{9}^{ecp}Ca_{16}^{ecp}}_{pc}$
terrace	T2	cluster	${Ca_8O_{20}Ca_{12}^{fix}Ca_{20}^{ecp}}_{pc}$
terrace	Т3	cluster	${Ca_{10}O_{26}Ca_{16}^{fix}Ca_{25}^{ecp}}_{pc}$
terrace	Т5	cluster	$\{Ca_{12}O_{38}Ca_{26}^{fix}Ca_{32}^{ecp}\}_{pc}$
step	MS2	cluster	$\{Ca_9O_{22}Ca_{13}^{fix}Ca_{21}^{ecp}\}_{pc}$
corner	C1	cluster	${Ca_{3}O_{7}Ca_{4}^{fix}Ca_{6}^{ecp}}_{pc}$
terrace	T1 _{pbc}	periodic	$p(2 \times 2 \times 6)$
terrace	T2 _{pbc}	periodic	$p(3 \times 3 \times 6)$
terrace	T3 _{pbc}	periodic	$p(4 \times 4 \times 6)$
step	MS1 _{pbc}	periodic	$p(2 \times 2 \times 6.5)$
step	MS3 _{pbc}	periodic	$p(4 \times 4 \times 6.5)$

"The subscript "pc" indicates the clusters are embedded in 2Dperiodic point charges. Ca atoms fixed at their lattice positions during structure optimizations are denoted "fix" for atoms described by basis functions and "ecp" for atoms described with ECPs. In the periodic models, half a unit indicates the topmost layer only covers half of the supercell to model monatomic step sites. shell of the clusters are Ca atoms fixed to their lattice positions. Successively larger cluster models T1, T2, T3, and T5 represent terrace sites. Cluster model MS2 represents a monatomic step site, and model C1 represents a corner site. The periodic models are constructed as supercells of primitive unit cells, with 1.0 nm of vacuum separating the CaO slab in the *z*-direction. The bottom two layers are frozen in their lattice positions during structure optimization. Periodic models $T1_{pbc}$, $T2_{pbc}$ and $T3_{pbc}$ represent terrace sites, and models MS1_{pbc} and MS3_{pbc} represent monatomic step sites.

Computational Methods. Density functional theory (DFT) calculations were performed with the B3LYP^{39,40} and PBE^{41,42} functionals using the computational package TUR-BOMOLE⁴³ and the Vienna ab initio simulation package (VASP).^{44,45} Cluster calculations were performed with the periodic electrostatic embedded cluster method (PEECM)⁴⁶ and fully periodic calculations were performed with the projector augmented-wave method (PAW).^{47,48} For the cluster calculations, a triple- ζ valence plus polarization (TZVP) basis set⁴⁹ was employed ("def2" in the TURBOMOLE library). For the periodic calculations, a plane-wave kinetic energy cutoff of 400 eV was used, and sampling of the Brillouin zone was restricted to the Γ point. Dispersive long-range corrections were added to the electronic energy with Grimme's D2 method,⁵⁰ where the C_6 and R_0 parameters of Ca^{2+} were assigned to the isoelectric Ar atom.⁵¹ The electronic energy barriers to adsorbed CO₂ rotation and oxygen lattice atom exchange were calculated by optimizing transition structures with the eigenvector following trust radius image minimization algorithm.^{52,53} Vibrational analyses were performed numerically with finite differences in the harmonic approximation.

Experimental Methods. The experiments were carried out in an ultrahigh vacuum (UHV) chamber equipped with low energy electron diffraction (LEED), scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) (all from Omicron), and an IR spectrometer (Bruker IFS 66v) for the IRAS measurements. The Mo(001) and Ru(0001)crystals (from MaTeck GmbH) were mounted on Omicron sample holders, with the temperature measured by a thermocouple spot-welded to the edge of the crystal. CaO(001) films about 5 nm in thickness were grown on Mo(001) and Ru(0001) crystals as described elsewhere.^{21,24} Briefly, Ca was deposited on clean metal substrates in 6×10^{-7} mbar of O_2 at 300 K, followed by UHV annealing at ~1200 K for ca. 5 min. Based on STM and LEED results,²¹ few point-like defects were observed on a single crystalline CaO(001) film on Mo(001). Considerable amounts of screw dislocations were observed; however the film was found to expose relatively wide terraces. The film prepared under similar conditions on a Ru(0001) substrate revealed poorly defined nanoparticles in granular-like films, which may, therefore, be considered as a polycrystalline CaO material.

The IRA spectra were recorded using p-polarized light at an 84° grazing angle of incidence (spectral resolution 4 cm⁻¹). CO_2 was dosed via backfilling the chamber to 10^{-8} mbar and then pumped before the IRAS measurements. Dosage and measurements were performed at room temperature. CO_2 exposures are given in Langmuirs (L), 1 L = 10^{-6} Torr s. As CO_2 was found to strongly adsorb on the CaO films,²¹ the

As CO_2 was found to strongly adsorb on the CaO films,²¹ the role of adsorption from residual gases can be neglected. In addition, the experiments presented here are limited to low dosages. Additional details of the computational and experimental procedures are given elsewhere.²¹

RESULTS AND DISCUSSION

Rotations. Since rotations of the carbonate species play a role in the oxygen exchange mechanisms, we discuss first only rotations. The oxygen atoms of the adsorbate on a terrace site can either point toward the lattice Ca^{2+} ions (0°) or be rotated 45° with respect to the surface, as shown in Figure 1.



Figure 1. Top-down views of adsorption structures of one CO_2 molecule (top) or two CO_2 molecules (bottom) on the CaO(001) terrace in the unrotated (left) or rotated (right) positions. Color code: red, O; gray, Ca; cyan, C. The atoms of CO_2 have been highlighted for clarity.

Calculations of the 45° rotated structure revealed stable minima with PBE on both the cluster and periodic models. With B3LYP, the rotated structure is also a local minimum on the periodic model and the largest cluster model studied. Furthermore, the cluster model calculations indicate that the 0° structure is the most stable species, whereas the periodic model calculations indicate that the 45° structure is the most stable. Other computational studies performed with DFT and interatomic potentials also predicted the 45° rotated structure to be the lowest energy species.^{17,18,54,55} Regardless of the true global minimum structure, the calculated energy differences are very small, as shown in Table 2.⁵⁶ Therefore, at room temperature, the single adsorbed carbonate species can be considered freely rotating.

Within carbonate pairs, chains, and other aggregates, the adsorbates are stable when the terminal oxygen atoms are rotated 45° with respect to the surface lattice structure. Individual carbonates within these oligomers can rotate 90° , sometimes forming new local minima. These rotated structures

can be found in Figures S2–S4 for three, four, and five terraceadsorbed carbonate species. The calculated minimum structure energy differences and barriers to rotation of these carbonates range from 0.4-11.4 kJ/mol, indicating that individual carbonates within aggregates can also rotate with relative ease.

Rotation of the adsorbed CO_2 at the monatomic step site was also considered. From the assignment that the energetically favorable step sites are completely filled even at the lowest experimentally observable coverage,²¹ we performed rigid scans of the rotation, i.e. without structural relaxation, for models of filled step sites (Figure 2a). The most favorable adsorption structures on step-edges form a zigzag pattern, where every other adsorbed CO_2 is either positioned nearly parallel to the surface or perpendicular to the surface (Figure 3). The stepedge binding motifs are denoted first and second, respectively, for these two adsorption geometries. For both binding motifs, a minimum energy is achieved at ~90° rotation angles, indicating the carbonates are aligned in parallel with the rim of the stepedge. The calculated barriers to rotation, ΔE^{\ddagger} , taken as the energy when the rotation angle is 0°, are given in Table 3.

For the cluster model MS2, adsorption of only two CO_2 molecules on the rim is possible due to the available adsorption sites. Given the additional degrees of freedom the adsorbates gain as a cluster-adsorbed pair, discrepancies among models are expected. To test if the energy of rotation is affected by our different models (i.e., cluster versus periodic), we compared the results on MS2-2CO₂ to MS3_{pbc}-2CO₂, the analogous periodic model. The energy profiles agree closely (see Figure S5), indicating the structure of the step-adsorbed pair, which differs slightly from structure of the completely filled step models, is the primary cause a lower rotational barrier of the CO₂ bound in the first structural motif.

Rigid scans in which the angle between the carbon of the carbonate and the step edge, called the bending angle, is modified are depicted in Figure 2b. The minimum bending angles for each binding motif, as well as the energy penalties to equate the bending angles of both adsorbates (called the bending energy), are listed in Table 3. From the relative bending energies, it is more energetically favorable for the CO_2 molecules to bind in the first motif than the second, even when there is steric crowding from neighboring adsorbates. The minimum bending angle of the adsorbates in the second binding motif (145–160°) is somewhat less than the bending angle of carbonates formed at terrace sites (180°). This is consistent with the ranking of stable adsorption sites from

Table 2. Calculated Energy Differences, ΔE (kJ/mol), and Energy Barriers, ΔE^{\ddagger} (kJ/mol), Due to Carbonate Rotations on CaO Terraces

		B3LYP+D ⁴		PBE+D ^a	
unrotated	rotated	ΔE	ΔE^{\ddagger}	ΔE	ΔE^{\ddagger}
T1-1CO ₂ (0°) T3-1CO ₂ (0°)	T1-1CO ₂ (45°) T3-1CO ₂ (45°)		2.0 $(1.4)^{b}$ 1.7 $(1.3)^{b}$	$0.7 (0.4)^{b}$	
T5-1CO ₂ (0°)	T5-1CO ₂ (45°)	1.5		1.0	
$T1_{pbc}$ -1 CO_2 (0°)	$T1_{pbc}$ -1 CO_2 (45°)	-1.2		-1.5	
$T2_{pbc}$ -1CO ₂ (0°)	$T2_{pbc}$ -1CO ₂ (45°)			-0.7	
$T3_{pbc}$ -1CO ₂ (0°)	$T3_{pbc}$ -1CO ₂ (45°)			-1.4	
T1-2CO ₂ (0°)	T1-2CO ₂ (90°)		9.3		9.7
$T2-2CO_2 (0^\circ)$	T2-2CO ₂ (90°)		11.4		

^aDFT+D single point calculation at the DFT structure. ^bValues in parentheses have zero-point vibrational energy included in the calculations.



Figure 2. Calculated relative energies of CO_2 (a) rotating and (b) bending on completely filled monatomic step models MS2 (B3LYP) and MS1_{pbc} (PBE) with rigid scans. The rotation angle is a torsional angle between a protruding oxygen of the carbonate with the step surface layer, shown in the top-down view of inset (a). The bending angle is between the carbon of the carbonate and the step edge, shown in the side view of inset (b). Color code of insets: red, O; gray, Ca; cyan, C.



Figure 3. Adsorption structures of CO_2 molecules on the CaO(001) monatomic step from side views of the step-edge. The material has been truncated for clarity. The CO_2 binding motifs have been labeled by "1st" and "2nd." Color code: red, O; gray, Ca; cyan, C.

empty step sites, to crowded step sites, followed by clean terrace sites.

The energy penalty for rotation on monatomic steps, however, is inversely related to the CO_2 bending angle. Therefore, CO_2 bound in the second motif (greater bending angle) requires much less energy for rotation than the first CO_2 (smaller bending angle), likely due to the steric interaction of the carbonate and the step surface layer. The greater energetic penalty for rotation at the monatomic step sites compared to the terrace suggests greater rigidity for the more strongly bound carbonates on rim sites.

Table 3. Energy Barriers to Rotation, ΔE^{\ddagger} (kJ/mol), Minimum Bending Angle (deg), and Bending Energy (kJ/mol) As Calculated by Rigid Structure Energy Scans of Completely Filled Monatomic Step Sites^a

	MS2-	2CO ₂	MS1 _{pbc} -2CO ₂		
adsorbed CO ₂	1st	2nd	1st	2nd	
rotation (ΔE^{\ddagger})	385.5	137.0	587.1	112.1	
bending angle	95	145	90	160	
bending energy ^b	52.8	33.4	177.6	75.5	

^{*a*}The cluster calculations were performed with B3LYP and the periodic calculations with PBE. ^{*b*}The bending energy is defined as the energy cost for the selected CO_2 to bend to the minimum bending angle of the other CO_2 .

Oxygen Scrambling. We calculated oxygen atom exchange transition structures for the terrace, monatomic step, and corner adsorption sites. The calculated energy diagrams for oxygen atom exchange on cluster models are plotted in Figure 4. The calculated energy barriers to oxygen atom exchange for all calculated models are given in Table 4, along with the calculated first-order rate constants (k) and half-life ($t_{1/2}$). The rate constants are calculated from transition state theory: $k = k_{\rm B}Th^{-1}\exp(-\Delta E^{\pm}/k_{\rm B}T)$, where $k_{\rm B}$ is Boltzmann's constant, T is the temperature (298.15 K), h is Planck's constant, and ΔE^{\pm} is



Figure 4. Calculated energy diagrams for the oxygen atom exchange mechanism on various morphological sites of CaO(001) with B3LYP. Relative energies are listed in parentheses in kJ/mol. (a) Terrace site, viewed in the (110) direction, with foreground atoms removed for clarity; (b) step site, viewed in the (100) direction; and (c) corner site, viewed in the (110) direction. Color code: red, O; gray, Ca; cyan, C. The models have been truncated, and the surface oxygen atom being exchanged is depicted in blue for clarity.

Table 4. Calculated Energy Barriers, ΔE^{\ddagger} (kJ/mol), Rate Constants, k (s⁻¹), and Half-Lifes, $t_{1/2}$ (s), of Oxygen Atom Exchange for a Single Carbonate Surface Species

*							
			ΔE^*				
	functional	DFT	DFT+D ^a	k	$t_{1/2}$		
$T1-1CO_2$ (TS)	B3LYP	126.7	133.5	2.5×10^{-11}	2.7×10^{10}		
$T1-1CO_2$ (TS)	PBE	127.9	132.7	3.5×10^{-11}	2.0×10^{10}		
$T1_{pbc}$ -1CO ₂ (TS)	PBE	109.6	113.8	7.2×10^{-8}	9.6×10^{6}		
$T1_{pbc}$ -2CO ₂ (TS)	PBE	116.0	122.6	2.1×10^{-9}	3.4×10^{8}		
$T1_{pbc}$ -4CO ₂ (TS)	PBE	141.5	148.0	7.3×10^{-14}	9.5×10^{12}		
$MS2-2CO_2 (TS)^b$	B3LYP	85.5	85.9	5.5×10^{-3}	1.2×10^{2}		
$MS1_{pbc}$ -2CO ₂ (TS) ^b	PBE	83.1	80.0	6.0×10^{-2}	1.2×10^{1}		
$C1-1CO_2 (TS)^c$	B3LYP	14.3	12.2	4.5×10^{10}	1.5×10^{-11}		
$C1-1CO_2 (TS)^d$	B3LYP	27.2	26.9	1.2×10^{8}	5.8×10^{-9}		

^{*a*}DFT+D single point calculation at the DFT structure. ^{*b*}Exchange is calculated for the carbonate in the 2nd binding motif. ^{*c*}This barrier describes the carbonate embedding into the corner via a screwing mechanism. See Figure 4c. ^{*d*}This barrier describes the carbonate removing from the corner via a screwing mechanism. See Figure 4c.



Figure 5. Calculated DFT+D relative adsorption energy in kJ/mol of CO_2 (black lines), intrinsic barrier to oxygen atom exchange (blue lines; see Table 4), and apparent barrier to oxygen scrambling (red lines), where the apparent barrier is the intrinsic barrier plus the adsorption energy. The diagram is divided into adsorption on terrace sites (left), step sites (middle), and corner sites (right).

the energy barrier. The half-life of a first-order reaction is calculated by $t_{1/2} = \ln(2)/k$.

The transition structure for oxygen atom exchange at a terrace site, T1-1CO₂ (TS), shown in Figure 4a, is rotated 45° with respect to the surface lattice and shows structural changes within the CaO surface layer. The ions closest to the carbonate have spread apart slightly, decreasing the repulsive interaction between the surface and the two proximate carbonate oxygen atoms (one of which came from the surface lattice). The calculated barrier to oxygen atom exchange using the cluster model is ~20 kJ/mol higher than on the analogous periodic

model. This difference, however, is negated when considering the apparent barrier rather than the intrinsic barrier (see below). The choice of functional does not appear to have a significant impact on the calculations. Upon aggregation on the terrace from an isolated carbonate, to a pair, and to a chain, the barrier to oxygen atom exchange increases from 114 to 148 kJ/ mol, likely due to crowding. We calculated the free energy barrier ΔG^{\ddagger} with B3LYP at 298.15 K and 1×10^{-8} mbar CO₂ for T1-1CO₂ to compare to the energetic barrier ΔE^{\ddagger} . The difference is only 0.8 kJ/mol, which imparts negligible changes to the calculated rate constant (1.9 \times 10 $^{-11}$ s $^{-1})$ and half-life (3.7 \times 10 10 s).

The transition structure for oxygen atom exchange within the step-adsorbed carbonate pair, MS2–2CO₂ (TS), is shown in Figure 4b. The CO₂ bound in the second adsorption motif appears rotated ~45° on the step-edge, which requires ~50 kJ/ mol based on the calculations in Figure 2a. In addition, the bending angle is slightly decreased, providing additional space for oxygen atom exchange despite an additional energetic cost. The calculated barrier to oxygen atom exchange with the periodic model MS1_{pbc} gives similar results to the cluster model, indicating that crowding at the step sites is less detrimental to oxygen atom exchange compared to terrace sites. Because rotation of the first CO₂ requires more energy than the second CO₂, it is expected that the barrier to oxygen atom exchange at the first binding motif would be higher in energy and is not calculated here.

The mechanism for oxygen atom exchange at a corner site differs slightly from that on terrace and step sites. Based on the calculated transition structure to oxygen atom exchange, C1- $1CO_2$ (TS), shown in Figure 4c, the corner surface oxygen atom is exchanged with an oxygen atom of adsorbed CO₂ via embedding of the carbonate unit into the lattice. While the embedded, pseudotridentate species C1-1CO₂ (A) is the calculated global minimum structure, there also exists the monodentate C1-1CO₂ (B) structure, 14.7 kJ/mol higher in energy. Rotation of the monodentate carbonate unit on the corner is not favored (~45 kJ/mol energy penalty for 90° rotation). However, there is a transition structure C1-1CO₂ (TS) only 12.2 kJ/mol higher in energy. The carbonate embedding mechanism resembles a screwing motion, whereby the carbonate twists 60°, simultaneously implanting itself into the corner of the CaO lattice. Repetition of this mechanism from C1-1CO₂ (A) to C1-1CO₂ (\overline{B}) and vice versa results in the oxygen atom exchange. The total calculated energy barrier for oxygen atom exchange on the corner site is only 26.9 kJ/ mol, significantly less than at step and terrace sites.

With the exception of the corner site, the calculated barriers have associated rate constants that are too small to occur with significant frequency, as shown by the calculated half-life times. However, the adsorption energy of CO_2 on clean CaO(001) terrace, step, and corner sites is extremely negative.²¹ Therefore, with one exception, the apparent barrier to oxygen atom exchange coupled with CO_2 adsorption is negative, as shown in Figure 5.

Isotopic Labeling Experiments. We performed adsorption experiments using ¹⁸O-labeled CO₂ to obtain further support for our previous assignments of the IRAS spectra.²¹ Four regions of the spectra can be assigned to various bending and stretching modes of monodentate surface carbonates: ν_{6} , asymmetric stretching; ν_{5} and ν_{4} , symmetric stretching; and ν_{3} , out-of-plane bending. These modes are depicted in Figure 6.

At the lowest exposure on the CaO/Mo system, shown in Figure 7a, the ν_5 peak at 1298 cm⁻¹ shifts by -30 cm⁻¹ to 1268 cm⁻¹. This peak corresponds to symmetric stretching of monodentate carbonates at completely filled step sites.²¹ The 1268 cm⁻¹ band is much broader and asymmetric after isotopic shifting, exhibiting a high frequency shoulder at 1281 cm⁻¹. The same band is also detected at the increased ~0.6 L exposure at 1267 cm⁻¹, with a corresponding satellite at 1280 cm⁻¹. Additional peaks at the ~0.6 L exposure have been assigned to the appearance of carbonates on terraces, either as pairs, chains, or larger aggregates.²¹ On the basis of signal ratios,



Figure 6. Vibrational modes of surface-adsorbed monodentate carbonates.

the 1311 cm⁻¹ peak shifts to 1292 cm⁻¹, while the shoulder at 1322 cm⁻¹ shifts to 1303 cm⁻¹. Thus, the observed -19 cm⁻¹ shifts for these bands, due to terrace-site adsorption of CO₂, are considerably smaller than ca. -30 cm⁻¹ obtained for the 1298 cm⁻¹ peak, due to step-site adsorption. A similar isotopic effect is observed for the low frequency mode, ν_4 . At ~0.1 L exposure, the 985 cm⁻¹ band red-shifts 26 cm⁻¹ to 959 cm⁻¹ and becomes asymmetric, similar to the 1268 cm⁻¹ band. At ~0.6 L exposure, similar shifting and broadening is observed.

Presuming the 1268 cm⁻¹ band is associated solely with vibrations in pure C¹⁸O₂, the observation of the 1281 cm⁻¹ band might be associated with vibrations involving both ¹⁸O and ¹⁶O, which would imply that C¹⁸O₂ exchanges an oxygen atom with Ca¹⁶O(001). We can rule out contamination of C¹⁸O₂ with mixed isotope C¹⁸O¹⁶O on the basis of observed signal intensity ratios. The higher frequency bands in the ~1300 cm⁻¹ region (ν_5) that gradually develop at higher exposures do not exhibit a satellite in the isotopic experiment, nor do the satellite peaks observed at the lowest exposure result in the same intensity ratios on CaO films grown on Mo compared to Ru.

Similar isotopic effects are observed on the CaO/Ru(0001) surface (Figure 7b). At the lowest exposure, the ν_5 peak at 1298 cm^{-1} transforms into a broad band peaked at 1280 cm^{-1} with a shoulder at 1266 cm⁻¹. While the peak positions are nearly identical as on the Mo substrate, the peak intensities are reversed. The 1280 cm⁻¹ peak appears double in intensity as the 1266 cm⁻¹ peak. Under the oxygen atom exchange paradigm, these results are consistent with more intense oxygen scrambling at the nanoparticulate CaO/Ru(0001) surface. At ~0.6 L exposure, peaks at 1640 (ν_6) and 875 (ν_3) cm^{-1} become visible that were unobserved in the CaO(001)/ Mo(001) experiments. These bands are only visible on CaO/ Ru(0001) films, due to a violation of the surface selection rules.²¹ While the ν_5 band centered at 1280 cm⁻¹ becomes too broad to perform a detailed deconvolution at ~0.6 L exposure, the other bands at 1640 (ν_6), 980 (ν_4), and 875 (ν_3) cm⁻¹ all red-shift by ca. 7, 35, and 6 cm⁻¹, respectively.

The relative intensities of the experimental peaks in the lowcoverage IRA spectra with C¹⁸O₂ dosing (Figure 7, top curves) suggest the species corresponding to the smaller ν_5 shift (ca. -17 cm^{-1}) in the experiment account for <30% of the total adsorbed CO₂ molecules on the Mo-grown film, and for >60% on the Ru-grown film. On the Mo-grown CaO(001) surface, the larger shift dominates; on the Ru-grown CaO surface, the smaller shift dominates. This suggests a greater degree of oxygen atom exchange on the disordered CaO/Ru(0001) surface. This could be due to the presence of more step and edge sites that have lower barriers to oxygen atom exchange than terraces, which is still consistent with the calculated IRA spectra of C¹⁶O₂.²¹ On edge sites with greater degrees of



Figure 7. IRA spectra of a $Ca^{16}O(001)/Mo(001)$ film (a) and a $Ca^{16}O(001)/Ru(0001)$ film (b) exposed to $C^{16}O_2$ (black lines) and $C^{18}O_2$ (red lines) at 0.1 L (top) and 0.6 L (bottom) exposures.

freedom than monatomic steps, CO_2 rotation is presumably less hindered, thereby facilitating oxygen atom exchange.

In conclusion, on $C^{18}O_2$ adsorption, we observe a splitting of the ν_5 band with shifts of -30 and -17 cm⁻¹, whereas the ν_4 band, which is difficult to accurately determine experimentally due to the limited peak intensity relative to noise, shifts by -26cm⁻¹. For the CaO/Ru film, the shifts to the red are 1 to 2 cm⁻¹ larger. These experimental values for ~0.1 L adsorption, as well as peak shifts at the higher ~0.6 L dosing, are compared to the calculated values in Tables 5 and 6 below.

Table 5. Calculated Isotopic Shifts of Frequencies (cm^{-1}) for the Adsorption of Two $C^{18}O_2$ Molecules Adsorbed to $Ca^{16}O$ Step Sites with PBE^{*a*}

	MS2-2	CO ₂	MS1 _{pbc} -2CO ₂		
case	$\Delta \nu_5$	Δu_4	$\Delta \nu_5$	Δu_4	
1	-31; -	-22	-34; -	-21	
2	-26; -	-27	-; -22	-26	
3	-27; -	-28	-; -22	-26	
4	-; -18	-27	-; -20	-25	
5	-; -17	-27	-; -19	-25	
6-9	-; -17	-34	-; -19	-31	
CaO/Mo	-30; -17	ca. –26	-30; -17	ca. –26	
CaO/Ru	-32; -18	ca27	-32; -18	ca27	

^{*a*}Shifts are calculated for the highest frequency ν_s mode and an average of the two ν_4 modes, based on the relative intensities of the calculated modes on MS2-2CO₂ after applying surface selection rules.

Wavenumber Calculations on Isotopically Substituted Models. We calculated wavenumbers for the adsorption of one, two, and three $C^{18}O_2$ molecules on terrace and step sites, corresponding to the proposed structures for lowcoverage CO₂ adsorption on CaO(001).²¹ For the adsorption of two $C^{18}O_2$ molecules, there exist nine possible structural configurations of oxygen atom exchange, as shown in Figure 8. In case 1, no ¹⁸O atoms from $C^{18}O_2$ have exchanged with surface oxygen atoms. In cases 2–5, a single ¹⁸O atom is exchanged from one $C^{18}O_2$ adsorbate. In cases 6–9, one ¹⁸O atom from each $C^{18}O_2$ is exchanged with surface ¹⁶O. For the adsorption of three $C^{18}O_2$ molecules, there are 27 unique adsorption cases, as shown in Figure S5. In many instances, however, cases are equivalent due to molecular symmetry of the adsorption structures.

Based on the assignments of the experimental IRAS spectra at low coverage, the isotopic shifts at ~0.1 L C¹⁸O₂ exposure are due to completely filled step sites.²¹ The calculated isotopic frequency shifts for carbonate pairs on monatomic step sites compared to experiment are given in Table 5. The calculated isotopic shifts of ν_5 of 2C¹⁸O₂ on cluster model MS2 in cases 1–3 agree well with the larger experimental shift of ca. –30 cm⁻¹ at the lowest coverage (Figure 7, top spectra). These cases correspond to either no oxygen atom exchange (case 1) or where a single oxygen atom is exchanged with the lattice from the CO₂ adsorbed in the first binding motif (cases 2–3). Cases 4–9 give a calculated shift in good agreement with the smaller experimental shift of ca. –17 cm⁻¹ at low coverage. These cases correspond to the configuration where either both

Table 6. Calculated Isotopic Shifts of Frequencies (cm^{-1}) for the Adsorption of Two $C^{18}O_2$ Molecules Adsorbed to $Ca^{16}O$ Terrace Sites with PBE^{*a*}

	$T2-2CO_2(0^{\circ})$				$T1_{pbc}-2CO_{2}$ (0°)			
case	Δu_6	Δu_5	Δu_4	$\Delta \nu_3$	$\Delta \nu_6$	Δu_5	Δu_4	Δu_3
1	-25	-33	-19	-6	-25	-31	-20	-7
2-5	-17	-23	-23	-6	-17	-22	-24	-7
6-9	-12	-18	-33	-6	-12	-17	-35	-6
CaO/Mo		ca19	ca23			ca19	ca23	
CaO/Ru	-7	ca28	ca35	-6	-7	ca28	ca35	-6

"Shifts are calculated for the highest frequency modes, based on the relative intensities of the calculated modes on T2-2CO₂ (0°) after applying surface selection rules.



Figure 8. Structural configurations of two $C^{18}O_2$ molecules adsorbed on CaO, including the possibility of oxygen exchange with the lattice: case 1 (no exchange); cases 2–5 (one oxygen exchange); and cases 6–9 (two oxygen exchanges). Side-view (left) depictions show the adsorbed carbonate pairs. Top-down (right) depictions show the carbonate oxygen atoms, where the central oxygen atom is embedded in the surface beneath the central carbon atom. The ¹⁶O atoms are shown in red for clarity.

CO₂ adsorbates undergo oxygen atom exchange with the lattice, or only the CO₂ adsorbed in the second binding motif. Fully filled step sites are not perfectly represented by adsorption of 2C18O2 on cluster model MS2, however. When considering the periodic model $MS1_{pbc}$ with $2C^{18}O_{\scriptscriptstyle 2\!9}$ the isotopic shifts in cases 2-3 more closely resemble the shifts of cases 4-9, as shown in Table 5. The difference in cases 2-3among models is demonstrated further by calculations with the larger periodic model, $MS3_{pbc}$, with $2C^{18}O_2$, given in Table S13. These data indicate that for completely filled step sites, any form of oxygen atom exchange gives an isotopic shift in ν_5 consistent with the smaller 17 cm⁻¹ red-shift observed in experiment. The observed shift of ν_4 agrees most with cases 2– 5 for any of the models studied, i.e, where a single oxygen atom within an adsorbate pair is exchanged. Therefore, it may be understood that a portion of the adsorbed CO2 molecules undergo oxygen atom exchange with the rim of the CaO step, in proportion to the observed signal ratios in the IRA spectra.

At the \sim 0.6 L dosing, both step and terrace site adsorption contribute to the IRA spectra.²¹ From the experimental spectra, the ν_5 peak at 1298 cm⁻¹ behaves similarly to the ~0.1 L exposure case. The additional peak on at 1311 cm⁻¹, however, shifts by -19 cm^{-1} based on the spectrum of CaO(001)/ Mo(001). This peak has been proposed to correspond to terrace-site carbonate pairs or chains.²¹ The calculated isotopic shifts of the carbonate pairs compared to experiment are given in Table 6. The calculations on the cluster model T2 agree well with the periodic model T1_{pbc}. With no oxygen atom exchange (case 1), the calculated isotopic shift in ν_5 is ca. -32 cm⁻¹, which is too large to be consistent with experiment. However, when considering oxygen atom exchange, the calculated isotopic shifts more closely resemble the experimental value. The trend in the calculated isotopic shifts in ν_4 is reversed compared to ν_5 : larger isotopic shifts are calculated for cases 6– 9 than for cases 1–5. The experimental shift in ν_4 of –23 cm⁻¹ (CaO on Mo) is consistent with cases 1-5 (no or one oxygen atom exchange), although the breadth of the peak indicates a wider margin of error.

The analogous ν_5 band of CaO/Ru(0001) shifts ca. -28 cm⁻¹, and the ν_4 band shifts ca. -35 cm⁻¹. These shifts are significantly larger compared with CaO/Mo. Comparing the calculated isotopic shifts to the CaO/Ru experimental values suggest that there is either no oxygen atom exchange (from the shift in ν_5) or double oxygen atom exchange (from the shift in

 ν_4), which is internally inconsistent. Overlapping peaks from the adsorption at steps may be a complicating factor in the interpretation of the results. Looking at the ν_6 and ν_3 peaks that are only visible in the Ru-supported CaO film, we find that ν_6 agrees best with experiment when considering oxygen atom exchange, and the shift in ν_3 seems to agree in all cases.

Finally, we also considered the effects of isotopic labeling on a short terrace-adsorbed carbonate chain (see Tables S17– S18). Similar to the carbonate pair on terraces, the calculated isotopic shift of ν_5 without considering oxygen atom exchange is -35 cm^{-1} , which is greater than the experimentally observed shift. When one carbonate unit undergoes oxygen atom exchange, the shift decreases in magnitude to -26 to -27cm⁻¹. When two or three carbonate units undergo oxygen atom exchange, the isotopic shift of ν_5 becomes -22 and -19 cm^{-1} , respectively. When considering a short chain of carbonates on terraces, the ν_4 band consists of two peaks. Each of the two ν_4 peaks shifts independently from the other upon isotopic labeling, further complicating the analysis. Shifts in the ν_6 and ν_3 peaks in carbonate chains are similar to those within the carbonate pairs.

From the above calculations, we hypothesize the necessity for oxygen scrambling on monatomic step and terrace sites to be consistent with the IRAS experiments. Furthermore, we propose that such oxygen atom exchange occurs from monodentate carbonate species on defect-free CaO(001) surfaces, rather than bidentate species or utilizing oxygen vacancies. A similar mechanism has been proposed for the exchange of lattice oxygen of MgO(001) with sulfur upon reaction with CS₂.⁵⁷ The computational study, which employed similar cluster models as in this work, did not involve bidentate structures. Despite the calculated exchange reaction barriers of 1.2, 2.2, 2.3, and 3.4 eV on a corner, step, edge, and terrace sites, respectively, the O/S exchange was corroborated experimentally. The smallest calculated O/S atom exchange on corner sites, 1.2 eV, is equivalent to the calculated intrinsic barrier to oxygen atom exchange between an isolated CO₂ and CaO(001) on a terrace site, providing additional support for our conclusion.

CONCLUSIONS

Our DFT calculations show that surface rotations of terraceadsorbed monodentate carbonate species are facile at room temperature, both as isolated species and within aggregates.

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Rotations at monatomic step sites are considerably more energy-intensive, due to the close interaction of the carbonate oxygen atoms with the step surface layer. When the step sites are completely filled, the adsorbates form a zigzag structure to avoid close interaction between neighbors. On corner sites, rotation of monodentate carbonates is not energetically favorable compared with the mechanism for embedding into the surface lattice structure, thereby facilitating an oxygen atom exchange.

The DFT calculations for isotopically substituted surface sturctures indicate that the IRA spectra of $C^{18}O_2$ on CaO(001) can be rationalized within the framework of the previous peak assignments by considering oxygen atom exchange with the $Ca^{16}O$ lattice. Calculations of electronic barriers for oxygen atom exchange show that oxygen scrambling is indeed easiest at corner sites (26.9 kJ/mol), larger at monatomic step sites (80 kJ/mol), and highest at terrace sites (113–148 kJ/mol). However, considering the strong adsorption energy of CO_2 on CaO(001), the apparent barrier to oxygen atom exchange into account, the calculated isotopic shifts in the IRA spectra are consistent with the experimental results, further validating our previous assignments of the IRA spectra.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b05293.

Calculated CO₂ adsorption energies; calculated frequencies of $C^{16}O_2$ adsorption; calculated frequencies of $C^{18}O_2$ adsorption; figures of adsorption structures; schematic of all possible oxygen atom locations within short terrace-adsorbed carbonate chains; optimized structures and energies (PDF)

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Notes

The authors declare no competing financial interest.

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