CO_2 Adsorption on $Ti_3O_6^-$: A Novel Carbonate Binding Motif

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S Supporting Information

ABSTRACT: CO₂ adsorption on $Ti_3O_6^-$, which serves as a model for an oxygen vacancy on a titania surface, is studied using infrared photodissociation (IRPD) spectroscopy in combination with density functional theory (DFT) and coupled cluster computations, as well as a recently developed multicomponent artificial force induced reaction method. The IRPD spectra of D₂-tagged $[(Ti_3O_6)(CO_2)_n]^-$, with n = 1, 2, are reported in the spectral window of 450-2400 cm⁻¹ and assigned based on a comparison to harmonic IR spectra from the DFT calculations. We find that CO₂ binding leaves the unpaired electron largely unperturbed. The first two CO2 molecules adsorb chemically to Ti₃O₆ by incorporating a



formally doubly negatively charged, either doubly or triply coordinated O atom to form a bidentate or tridentate bridging carbonate dianion (CO_3^{2-}) , respectively. The latter binding motif exhibits a characteristic IR signature in the form of an intense doublet of peaks near 1400 cm⁻¹ stemming from two antisymmetric carbonate stretching modes.

1. INTRODUCTION

Steadily growing global energy consumption has led to a sharp rise in atmospheric CO_2 levels, one of the factors contributing to anthropogenic climate change. Hence, there is an increasing demand for efficient methods to reduce atmospheric CO₂ and convert it into value-added chemicals using heterogeneous catalysts.^{1,2} TiO₂-based materials have been identified as promising, cost-efficient candidates for CO₂ sequestration and conversion, considering their relative abundance in earth's crust in combination with their photocatalytic activity.^{3–5} To enhance the photocatalytic efficiency, it is necessary to develop an understanding of the fundamental processes occurring at the TiO₂ interface. Adsorption studies of CO₂ on titania, for example, have focused on a molecular level characterization of chemi- versus physisorption, that is, formation of bicarbonate or carbonate versus CO₂ binding exclusively to a metal center through one of its oxygen atoms, and are typically discussed in the context of Lewis acids and bases, finding that stronger CO_2

binding is promoted by higher oxygen basicity as well as higher metal acidity.⁶⁻⁹ Here, we employ a complementary approach to shed new light on TiO_2-CO_2 interactions. We use infrared photodissociation (IRPD) spectroscopy, combined with density functional theory (DFT) calculations, to study CO₂ adsorption by the radical anion $Ti_3O_6^-$ in the gas phase. This cluster represents a model for oxygen vacancies on titania surfaces.¹⁰ The goal of the present study is identifying the vibrational signatures of characteristic binding motifs in the vicinity of such defect sites.

The C_s structure of Ti₃O₆⁻ (see Figure 1), characterized previously by IRPD spectroscopy,10 exhibits two 4-fold coordinated Ti⁴⁺ centers and one triply coordinated Ti³⁺

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Figure 1. Spin density plot of the singly occupied molecular orbital in the $Ti_3O_6^-$ anion from ω B97XD/aug-cc-pVTZ calculations. The unpaired electron is localized at the under coordinated Ti^{3+} center. Bond lengths (in pm) are also shown.

center. The latter carries the spin density and represents the reactive center for hydrogen dissociation¹¹ as well as water adsorption.¹² CO₂ adsorption could be favorable at this site as it represents an electron donor site for the π acceptor CO₂. However, there are many possible binding motifs known from CO₂ adsorption studies on titania surfaces^{7,8,13,14} and on neutral and small anionic titanium oxide clusters in the gas phase.^{15,16} These include chemisorbed monodentate, bridging bidentate, chelating bidentate and tridentate carbonates, oxalates, as well as configurations with linear and bent physisorbed CO₂. A priori, it is unclear which binding motifs are preferred in the $[Ti_3O_6(CO_2)_n]^-$ system. Our results show that two types of tridentate carbonates, each with its own characteristic IR signature, are formed, an asymmetric and a symmetric one, of which the latter has not been reported previously.

2. EXPERIMENTAL AND COMPUTATIONAL METHODS

Experimental Methods. The IRPD experiments were carried out with an ion trap tandem mass spectrometer described previously.^{17,18} In brief, $[Ti_3O_6(CO_2)_n]^-$ (n = 1, 2) clusters are produced in a dual gas channel pulsed laser-vaporization source operated at 50 Hz.^{11,19} The beam of ions

passes through a 4 mm diameter skimmer and is collimated in a radio frequency (RF) decapole ion-guide filled with He buffer-gas. Ions of interest are mass-selected according to their mass/charge ratio using a quadrupole mass-filter (see Figure S1 for a characteristic mass spectrum of the $[Ti_3O_6(CO_2)_n]^$ clusters studied here). The mass-selected beam is focused into a cryogenically cooled RF ring-electrode ion trap. The trap is continuously filled with buffer gas (10% D_2 in He) at a trap temperature of 13-15 K, which allows for the accumulation and thermalization of the trapped ions. Inside the trap, ions undergo three-body collisions with the buffer gas, which promote the formation of weakly bound ion-D₂ complexes.²⁰ Ions are extracted from the ion trap at 5 Hz and are focused into the center of the extraction region of a time-of-flight (TOF) mass spectrometer, where they are irradiated by an intense and wavelength-tunable IR laser pulse from the IR free electron laser FHI FEL.²¹ When resonant with a rovibrational transition, the initially internally cold parent ions can absorb one (or more) photon(s), leading to loss of messenger molecules via intramolecular vibrational predissociation. At sufficiently high pulse energies, loss of the more strongly bound CO₂ molecules is also observed.

The TOF intensities of all ions are monitored simultaneously as the FEL wavelength is scanned from 450 to 2400 cm⁻¹ in 3 cm⁻¹ steps; for each wavelength step, ~100 TOF traces are acquired and averaged. Over this wavelength range, the FHI FEL has a spectral bandwidth ranging from 2 cm⁻¹ fwhm at 450 to 7 cm⁻¹ fwhm at 1200 cm⁻¹, and a typical energy output of 10–30 mJ/pulse. Attenuated laser pulses using 12–33% of the full FEL power are employed in a particular spectral window to ensure operation within a linear absorption regime and to avoid saturation. Typically, at least three scans are summed, the photodissociation cross section $\sigma_{\rm IRPD}$ is determined as described previously,^{22,23} and the data obtained in separately scanned ranges are stitched together to obtain the final IRPD spectrum.



Figure 2. Experimental IRPD spectra of D_2 -tagged $[Ti_3O_6 (CO_2)_n]^-$ with n = 0, 1 and 2. See Table 2 for band positions and assignments. Four characteristic spectral regions are indicated by the dashed lines: (i) antisymmetric O–C–O stretching modes (>1000 cm⁻¹), (ii) symmetric O–C–O and terminal Ti–O stretching modes (1000–900 cm⁻¹), (iii) stretching modes associated with Ti–O–Ti bridges and O–C–O bending modes (900–600 cm⁻¹), and (iv) low frequency bending, wagging, rocking, and ring breathing modes (<600 cm⁻¹).

Computational Methods. DFT calculations were carried out using the Gaussian 09 (rev. C01) program package²⁴ to find relative energies, optimized geometries, BSSE-corrected binding energies, harmonic vibrational frequencies, and IR intensities of the lowest-lying $[Ti_3O_6(CO_2)_{n=1-2}]^-$ isomers. We use the range-separated hybrid ω B97X-D functional²⁵ which includes dispersion interactions. It has been shown to perform well for geometry optimization of transition metal compounds²⁶ and has provided satisfactory results in our previous work on $[(TiO_2)_{n=2-4}(D_2O)_{m=1-3}]^{-12}$ The aug-cc-pVTZ basis set^{27,28} was used for all atoms, with full treatment of all electrons.

Single point CCSD(T) calculations^{29–33} of all the lowest lying isomers (for n = 2 aug-cc-pVDZ optimized geometries were taken for CCSD(T) calculation) were performed with the def2-TZVP^{34,35} basis set using the TURBOMOLE 6.6 programs.³⁶ In the search of energetically low-lying structures of bare and D₂-tagged $[Ti_3O_6(CO_2)_{n=1-2}]^-$ isomers, the multicomponent artificial force induced reaction (MC-AFIR) method implemented in the GRRM program was used,³⁷³⁸ where geometries obtained by the MC-AFIR calculations utilizing the PBE functional and DZP basis set of the SIESTA program³⁹ were reoptimized at the aforementioned computational level using Gaussian 09 (rev. C01).²⁴

3. RESULTS

The experimental IRPD spectra of the D2-tagged anions $[Ti_3O_6 (CO_2)_n]^-$, with n = 0-2, are shown in Figure 2 in the spectral region 450-2400 cm⁻¹. Experimental band positions and band assignments (vide infra) are summarized in Table 1. Based on our previous studies of titanium oxide anions^{10,12} and CO₂ adsorption,⁴⁰ we group characteristic normal modes into four spectral regions, labeled (i) to (iv) in Figure 2: (i) antisymmetric O–C–O stretching modes (>1000 cm⁻¹), (ii) symmetric O-C-O and terminal Ti-O stretching modes $(1000-900 \text{ cm}^{-1})$, (iii) the stretching modes associated with Ti-O-Ti bridges and O-C-O bending modes (900-600 cm⁻¹), and (iv) low frequency bending, wagging, rocking, and ring breathing modes (<600 cm⁻¹). No evidence is found for the IR signature of physisorbed CO2, which would be above 2000 cm⁻¹, close to the absorption of neutral CO_2 (2349 cm^{-1}).⁴¹

The IRPD spectrum of D₂-tagged $[\text{Ti}_3O_6(\text{CO}_2)_n]^-$ for n = 0 has been discussed in detail previously.¹⁰ Briefly, no absorption is observed in the region (i). The two characteristic peaks in region (ii) are the symmetric $(a_1, 972 \text{ cm}^{-1})$ and antisymmetric $(a_2, 948 \text{ cm}^{-1})$ terminal Ti–O stretching modes. Six vibrational bands that show decreasing IR intensity with decreasing frequency are observed below 750 cm⁻¹ and attributed to Ti–O–Ti bridge stretching modes.

The IRPD spectrum for n = 1 (center panel in Figure 2) looks similar to that for n = 0 below 950 cm⁻¹, suggesting that the core structure remains intact upon adsorption of the first CO₂ molecule. The signal-to-noise ratio is slightly better in the present spectra (n = 1, 2) compared to the previously published one (n = 0), mainly a result of improved source conditions.¹⁰ The intense peaks observed above 950 cm⁻¹ at 1773 cm⁻¹ (b₁), 1144 cm⁻¹ (b₂), and 984 cm⁻¹ (b₃) signal that CO₂ is preferentially chemisorbed. This particular carbonate stretch pattern, with no absorption in the 1200–1600 cm⁻¹ region, fits best with a bridging bidentate carbonate species,^{7,8} as discussed in more detail in Section 4. There is a weak

Table 1. Experimental Band Positions (in cm⁻¹) from the IRPD Spectra of D₂-Tagged $[Ti_3O_6 (CO_2)_n]^-$, Shown in Figure 2, and ω B97XD/aug-cc-pVTZ Harmonic Frequencies Scaled by 0.96 (in cm⁻¹) of Isomers 1b (n = 1) and 2a (n = 2), as Well as Band Assignments

n	label	experiment	(cm^{-1})	assignment
1	1	(em)	17(1	
1	b ₁	1//3	1/61	terminal C=O stretch
	b ₂	1144	1157	antisym. CO_2 stretch
	b ₃	984	1017	sym. CO_2 stretch
	b ₄	954	993	terminal Ti–O stretch (sym.)
	b ₅	936	965	terminal Ti–O stretch (antisym.)
	b_6	813	748	in-plane CO ₃ bend
	b ₇	780	726	antisym. Ti–O–Ti ring stretch
	b_8	747	692	antisym. ring breathing
	b ₉	693	656	in-plane CO ₃ bend
	b_{10}	630	614	O–(Ti) ₃ stretch
	b ₁₁	561	565	$O-(Ti)_3$ bend
2	c ₁	1779	1778	terminal C=O stretch
	c ₂	1400	1415	antisym. CO ₃ stretch
	c ₃	1391	1382	antisym. CO ₃ stretch
	c ₄	1147	1155	antisym. CO ₂ stretch
	c ₅	1052	1048	sym CO ₃ stretch
	c ₆	994	1022	terminal Ti–O stretch (sym.)
	c ₇	976	994	terminal Ti–O stretch (antisym.)
	c ₈	947	954	sym. CO ₂ stretch
	c ₉	867	874	CO ₃ umbrella motion
	c ₁₀	806	776	antisym. Ti–O–Ti ring stretch
	c ₁₁	767	756	in-plane CO ₂ bend
	c ₁₂	684	672	antisym. Ti–O–Ti ring stretch
	c ₁₃	653	651	in-plane CO ₂ /CO ₃ bend
	c ₁₄	612	602	sym. Ti–O–Ti ring stretch
	c ₁₅	530	530	antisym. ring breathing
	c ₁₆	491	484	antisym. ring breathing

feature at 2285 cm⁻¹, indicative of another isomer containing a physisorbed CO₂, but its contribution is negligible.

The IRPD spectrum for n = 2 (bottom panel in Figure 2) shows similarities to the n = 1 spectrum over large parts of the spectral range. The carbonate stretching bands c_1 , c_4 , and c_6 in the n = 2 spectrum are found nearly unshifted from the positions in the n = 1 spectrum, where they correspond to bands b_1 , b_2 , and b_3 . The persistence of these bands supports an identical bridging bidentate binding motif for one of the two CO₂ molecules in the n = 2 species. There are, however, two new, closely spaced features at 1400 cm⁻¹ (c_2) and 1391 cm⁻¹ (c_3) that cannot be attributed to any of the known CO₂ binding motifs,^{7,8} including those proposed in a recent computational study on neutral Ti₃O₆ (CO₂)_n clusters.¹⁵

4. ANALYSIS AND DISCUSSION

In order to assign the IRPD spectra, we performed geometry optimizations and harmonic frequency calculations using DFT. The ω B97XD/aug-cc-pVTZ relative electronic energies $\Delta E_{\rm DFT}$ and zero-point energy (ZPE) corrected relative energies $\Delta E_{0,\rm DFT}$ are listed in Table 2. To obtain more accurate electronic energies, we also calculated CCSD(T)/def2-TZVP single-point energies $\Delta E_{\rm CCSD(T)}$ at the optimized ω B97XD/ aug-cc-pVTZ geometry; these are also listed in Table 2. The six

Table 2. ω B97XD/aug-cc-pVTZ Relative Electronic Energies ΔE_{DFT} and ZPE-Corrected Relative Energies $\Delta E_{0,\text{DFT}}$ of the Lowest-Energy Minimum-Energy Isomers of $[\text{Ti}_{3}\text{O}_{6} (\text{CO}_{2})_{n=1.2}]^{-a}$

n	isomer	$\Delta E_{\rm DFT}^{b}$	$\Delta E_{0,\mathrm{DFT}}^{c}$	$\Delta E_{\text{CCSD}(T)}^{b}$	$\Delta E_{0,\mathrm{CCSD}(\mathrm{T})/\mathrm{DFT}}^{c}$
1	1a	0.0	0.0	0.0	0.0
	1b	19.1	18.0	0.0	-0.8
	1c	12.0	11.9	10.5	11.2
	1d	37.4	39.2	81.7	84.4
	1e	45.1	38.2	156.0	149.9
	1f	53.4	46.2	130.2	123.8
2	2a	0.0	0.0	0.0	0.0
	2b	18.5	17.8	14.9	14.2
	2c	24.5	24.2	41.8	41.6
	2d	32.5	30.6	27.4	25.4
	2e	39.2	38.8	75.4	75.1
	2f	41.4	40.1	47.5	46.2

^{*a*}CCSD(T)/def2-TZVP relative electronic energies $\Delta E_{\text{CCSD}(T)}$ at the DFT minimum-energy geometry and ZPE-corrected relative electronic energies $\Delta E_{0,\text{CCSD}(T)/\text{DFT}}$ using the DFT ZPE-correction are also shown. All energies are given in kJ/mol. ^{*b*}Absolute energies: -3189.03837 au (1a, DFT), -3182.85095 au (1a, CCSD(T)), -3377.67800 au (2a, DFT), -3370.61920 au (2a, CCSD(T)). ^{*c*}Zeropoint-energy (ZPE) determined from ω B97XD/aug-cc-pVTZ harmonic vibrational frequencies.

lowest minimum-energy structures for n = 1 and n = 2 are shown in Figure 3. The isomers are labeled with nx, where n is the number of CO₂ molecules adsorbed to Ti₃O₆⁻ and x = a, b, c, ... indicates the energetic ordering. See Tables 2 and S3 for the isomer energies and Figures S2 and S3 for the harmonic IR spectra of all the considered isomers.

For $[Ti_3O_6.CO_2]^-$, we considered the six structures (1a-1f)shown in Figure 3. Their relative energies are listed in Table 2. Chemisorption, that is, carbonate formation (1a-1d), is preferred over physisorption, with a counterpoise-corrected DFT CO₂ binding energy of 139 kJ/mol (1a). Note that the physisorbed complexes (1e, 1f) are predicted to lie even higher in energy when the CCSD(T) energies are considered (see Table 2). Structure 1a represents the global minimum-energy structure using DFT. Structure 1b is predicted to be 19 kJ/mol higher in energy. However, when the CCSD(T) energies are considered, structures 1a and 1b are nearly isoenergetic, with 1b predicted only +0.3 kJ/mol higher in energy. Moreover, when the harmonic vibrational ZPEs from DFT are combined with the CCSD(T) electronic energies, the energetic ordering is reversed and 1b is indeed slightly favored by 0.8 kJ/mol. Both of these structures exhibit carbonate binding motifs, but in different binding environments and with different formal charges on the carbonate moiety: -1.039 lel (1a) versus -1.126 lel (1b) (see Figure S6 and Table S1). Structure 1a contains a tridentate, quasi-symmetric carbonate moiety, $(C(-O)_3)^{2-}$, that exhibits three similar C-O bonds (~131 pm, see SI) and forms three Ti-O bonds, one to each of the three Ti centers. On the other hand, 1b contains an asymmetric tridentate carbonate moiety, $(O=C(-O)_2)^{2-}$, that involves a bridging O atom and only two Ti-centers. The higher energy chemisorbed structures involve an asymmetric bidentate carbonate species bound to a single Ti-center (1c, $\Delta E_{\text{CCSD}(T)} = 11 \text{ kJ/mol}$ and a quasi-symmetric tetradentate carbonate species bound to two Ti-centers involving a bridging O atom (1d, +82 kJ/mol). Dixon and co-workers¹⁵ find structures similar to 1b to 1d for neutral chemisorbed



Figure 3. ω B97X-D/aug-cc-pVTZ minimum-energy structures, symmetry (in parentheses) and relative CCSD(T) single-point energy (in kJ·mol⁻¹) of energetically low-lying $[Ti_3O_6 (CO_2)_{n=1,2}]^-$ isomers. The ZPE-corrected energies are given in parentheses. The isomers are labeled with *nx*, where *n* is the number of CO₂ molecules adsorbed and *x* = **a**, **b**, **c**, ..., which indicates the energetic ordering. Atoms in gray represents Ti, dark gray represents C, red represents O, and blue represents H. The structures of D₂-tagged species for **1a**, **1b**, and **2a** are also shown.

 $[Ti_3O_6(CO_2)]$ clusters of which the neutral structure corresponding to 1d was found to be the lowest in energy. Interestingly, they did not consider the tridendate symmetric carbonate motif of 1a. We determined the optimized geometry of the neutral analogue of 1a and find that it lies 20 kJ/mol above the 1d analogue using DFT (see Table S1). However, when the CCSD(T) energies are considered, the order is reversed; the 1a analogue is predicted 11 kJ/mol below the 1d analogue and thus is likely the ground state structure of neutral $[Ti_3O_6(CO_2)]$. Formation of the physisorbed species 1e (+130 kJ/mol) and 1f (+156 kJ/mol) is less favorable compared to the corresponding neutral clusters and contain bent CO_2 moieties (see SI for geometric parameters), indicating partial charge transfer to the CO_2 .

Messenger-tagging with D_2 also plays a significant role for the energetic ordering of the isomers. We calculated counterpoise-corrected D_2 binding energies for $1a \cdot D_2$ and $1b \cdot D_2$ and find that 1b (21 kJ/mol) binds D_2 more than twice as strong as 1a (9.0 kJ/mol). This is presumably due to the higher positive atomic charge on the corresponding Ti atom in 1b (0.86 lel)versus 1a (0.59 lel). Hence, messenger tagging favors the formation of $1b \cdot D_2$.

For n = 2, we considered the six structures shown in Figure 3. Their relative DFT and CCSD(T) energies are listed in Table 2. Independent of the computational method used, 2a is

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predicted to lie lowest in energy followed by 2b, which lies about 15 kJ/mol higher. Structure 2a consists of two chemisorbed CO₂ molecules in the form of a bidentate (1b) and tridentate (1a) bridged carbonate, the two most stable n = 1 motifs. Structure 2b corresponds to the combination of the 1b/1c motifs, while the higher energy isomers 2d (+27 kJ/ mol), 2c (+42 kJ/mol), and 2e (+75 kJ/mol) then represent the 1b/1b, 1c/1c, and 1b/1d combinations, respectively. Structure 2f (+48 kJ/mol) exhibits similar CO₂ binding motifs as 2b, but here the two carbonate groups share a Ti⁴⁺ center.

In order to assign the IRPD spectra of the D₂-tagged $[Ti_3O_6(CO_2)_n]^-$ anions with n = 1 and 2, we compare them to the calculated harmonic spectra of the three lowest energy isomers (without tag) in Figures 4 and 5, respectively (see Figures S2



Figure 4. Experimental IRPD and IRMPD spectra of D₂-tagged $[Ti_3O_6(CO_2)]^-$ and calculated IR spectra of the three energy isomers (1a-1c) of the untagged anions. The IRPD spectrum (top panel), measured with an attenuated (14%) laser beam, shows the D₂-loss channel, while the IRMPD spectrum (second panel from top), measured with a nonattenuated laser beam, shows the CO₂-loss channel. The calculated IR spectra (lower panels), derived from ω B97XD/aug-cc-pVTZ harmonic frequencies (scaled by 0.96) and intensities, are plotted with sticks (gray) and a 10 cm⁻¹ fwhm Gaussian line shape convolution. See Table 1 for band assignments.

and S3 for a comparison to the spectra of all isomers, also including isomers with D_2 tag). For n = 1 (see Figure 4), we find the best agreement of the experimental D2-loss IRPD spectrum with the simulated spectrum of 1b. It reproduces all of the observed bands b_1 to b_{11} satisfactorily (see Table 1). The three absorption bands b_1 (1773 cm⁻¹), b_2 (1144 cm⁻¹), and b_3 (984 cm⁻¹) are assigned to the terminal C=O (1761 cm⁻¹), antisymmetric CO₂ (1157 cm⁻¹), and symmetric CO₂ (1017 cm^{-1}) stretching modes, respectively, of the bridging bidentate carbonate moiety. Bands b_4 (954 cm⁻¹) and b_5 (936 cm^{-1}) correspond to the symmetric (993 cm^{-1}) and antisymmetric (965 cm⁻¹) combinations of the terminal Ti-O stretching modes, followed by CO_3 bending (b_6, b_9) and Ti-O-Ti stretching and bending modes at lower energies. Note that the weak features at 1855 and 1174 cm⁻¹ (marked with an asterisk in Figure 2) are not reproduced by the harmonic spectrum and we therefore attribute them to



Figure 5. Experimental IRPD spectra of D₂-tagged $[Ti_3O_6 (CO_2)_2]^-$ (top panel) and calculated IR spectra (lower panels) of the three lowenergy isomers (**2a-2c**) of the untagged anions. The calculated IR spectra, derived from ω B97XD/aug-cc-pVTZ harmonic frequencies (scaled by 0.96) and intensities, are plotted with sticks (gray) and a 10 cm⁻¹ fwhm Gaussian line shape convolution. See Table 1 for band assignments.

excitation of antisymmetric CO_2 stretching mode/triply coordinated O atom stretching mode and carbonate bending mode/ring breathing mode combination bands, respectively. The spectrum of **1c**, on the other hand, does not reproduce the characteristic triplet b_3-b_5 around 1000 cm⁻¹, because one of the Ti=O sites is occupied. The spectrum of **1a** exhibits two characteristic antisymmetric stretching modes of the symmetrically bound carbonate species at 1436 and 1350 cm⁻¹, which are not observed in the D₂-loss channel.

Interestingly, we do find evidence for the population of (bare) 1a when monitoring the CO_2 -loss channel as part of IRMPD measurements using higher pulse energies (~8 vs 1 mJ). In addition to the features previously attributed to 1b, the corresponding IRMPD spectrum (see second trace from top in Figure 4) exhibits two weaker peaks at 1427 (b₂") and 1329 cm⁻¹ (b₃"), which we assign to the two antisymmetric stretching modes of the tridendate carbonate in 1a. This observation confirms that 1a lies close in energy to 1b in the absence of tagging and both are formed and present initially in the ion trap, but subsequent D₂-tagging then favors the formation 1b-D₂ over 1a-D₂.

The IRPD spectrum of the n = 2 cluster is compared to the harmonic spectra of the three lowest energy isomers in Figure 5. Only the spectrum of the lowest energy isomer **2a** reproduces the characteristic IR signature in the C–O stretching region. The four bands at 1779 (c₁), 1400 (c₂), 1391 (c₃) and 1147 cm⁻¹ (c₄) are assigned to the terminal C=O (1778 cm⁻¹) and antisymmetric CO₂ stretch (1155 cm⁻¹) of the bidentate carbonate as well as the two antisymmetric CO₃ stretches (1415 and 1382 cm⁻¹) of the tridentate carbonate. Note that the calculated splitting of the antisymmetric CO₃ stretches of 33 cm⁻¹ for the untagged cluster (spectrum **2a** in Figure 5) is substantially larger than the experimental value of 9 cm⁻¹ (for the tagged cluster), but is

reduced to 2 cm⁻¹ when D₂-tagging is explicitly considered (see Figure S3). This is the only band that shows such a pronounced messenger-tag induced shift. The bands at lower energies can then be assigned as follows. Bands c_5 (1052 cm⁻¹) and c_8 (947 cm⁻¹) are the symmetric CO₃ (1048 cm⁻¹) and CO_2 (954 cm⁻¹) stretches of the tridentate and bidentate bridging carbonates, respectively. The symmetric (1022 cm^{-1}) and antisymmetric (994 cm⁻¹) combinations of the terminal Ti–O stretches correspond to bands $c_6 \ (994 \ cm^{-1})$ and c_7 (976 cm⁻¹), followed by Ti–O–Ti ring stretching (c_{10},c_{12}) , CO_3/CO_2 bending modes (c_{9},c_{11},c_{13}) , and Ti-O-Ti ring breathing modes $(c_{14}-c_{16})$ at lower energies (see Table 1). The spectra of 2b and 2c, on the other hand, cannot recover the experimental spectrum, in particular the characteristic doublet of the tridentate carbonate moiety around 1400 cm⁻¹ (c_2 , c_3) is absent from these spectra.

The similarities in the IRPD spectra of D₂-tagged [Ti₃O₆ $(CO_2)_{0-2}$ ⁻ anions show that addition of up to two CO_2 molecules to Ti₃O₆⁻ leads to local perturbations rather than overall structural changes. For example, the two terminal Ti=O bonds remain intact and slightly increase in bond strength upon CO2 addition, indicated by a small, but consistent, blue-shift of the corresponding stretching modes from 970/948 cm⁻¹ (n = 0) to 984/954 cm⁻¹ in the n = 1cluster and 994/976 cm⁻¹ in the n = 2 cluster, concomitant with a predicted shortening of the terminal Ti-O bonds from 164 pm (n = 0) to 162 pm (n = 2). Similarly, the two stretching modes associated with the bidentate carbonate species are also slightly blue-shifted from $1773/1144 \text{ cm}^{-1}$ (*n* = 1) to $1779/1147 \text{ cm}^{-1}$ (*n* = 2). The spectral changes in regions (iii) and (iv) ($<900 \text{ cm}^{-1}$) are slightly more pronounced, but also not dramatic. Finally, calculation of the spin density for the n = 0-2 anions (see Figure S5) confirms that the localized, unpaired electron remains nearly unperturbed upon CO₂ adsorption. On the other hand, D2-tagging leads to more substantial effects, for example, the symmetric CO₂ stretch in the spectrum of 1b is red-shifted by 61 cm⁻¹ and its IR intensity increases by a factor of 6 (from 99 to 626 km/mol) upon D_2 -tagging (see Figure S2) as a result of electron delocalization from the Ti^{3+} center to the D_2 molecule.

5. CONCLUSIONS

In summary, we find that the first two CO_2 molecules adsorb chemically to $Ti_3O_6^-$, leaving the unpaired electron largely unperturbed. CO_2 activation in this case involves the incorporation of a formally doubly negatively charged, either doubly or triply coordinated O atom to form a bidentate or tridentate bridging carbonate dianion (CO_3^{2-}) , respectively. The bidentate binding motif described here is well-known from CO_2 adsorption studies on TiO_2 anatase surfaces^{7,8,13,14} and has also been predicted as a particular stable motif for CO_2 adsorption on neutral gas phase titanium oxide clusters.¹⁵ The tridentate binding motif is identified here experimentally for the first time and exhibits a characteristic IR signature in the form of an intense doublet of peaks near 1400 cm⁻¹, which correspond to two antisymmetric carbonate stretching modes.

The present results have several implications for understanding CO_2 activation/conversion in general and CO_2 adsorption at titania interfaces in particular. For example, the characterization of the role of bicarbonate (HCO₃⁻) species in such processes using IR spectroscopy may require additional scrutiny, since the characteristic doublet of the tridentate carbonate binding motif lies in the same spectral region that has typically been attributed to HCO₃^{-.8,14} Moreover, recent DFT calculations suggest that a tridentate binding motif plays a central role in the oxygen exchange mechanism on a defective anatase surface.⁴² However, the prediction of the reaction barriers for such rather complex systems using DFT depends intimately on the specific value of the Hubbard U correction used to describe the on-site Coulomb interaction.^{43,44} Gas phase clusters such as those studied here represent ideal model systems to accurately test more such approximate computational methods, since smaller clusters are amenable to higher level calculations.^{19,45,46}

The present study also demonstrates the high potential of calculations based on the AFIR method for investigation of chemical reactions on small atomic clusters. In future IRPD studies, we will try to obtain a molecular level understanding of how water coadsorption influences CO_2 activation in these model systems and how this ultimately can be exploited for the catalytic conversion of CO_2 to value-added chemicals.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b10724.

Quadrupole mass spectra; experimental spectra compared to computed spectra for all the isomers; additional possible isomers, spin densities, and NBO charges; isomer energies; Cartesian atomic coordinates of all calculated isomers (PDF).

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Notes

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