Matrix Infrared Spectra and Density Functional Calculations of TiO_3 and TiO_5 in Solid Argon

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The reaction of titanium monoxide molecules and O_2 was studied by using matrix isolation infrared spectroscopy as well as theoretical calculations. The titanium monoxide molecule reacts with O_2 to form TiO_3 spontaneously on annealing. The TiO_3 molecule is characterized to be a side-on bonded peroxo titanium monoxide complex, $(\eta^2\text{-}O_2)TiO$, which has a nonplanar C_s symmetry with a $^1A'$ ground state. The $(\eta^2\text{-}O_2)TiO$ complex can further coordinate another dioxygen to give TiO_5, a disuperoxo titanium monoxide complex, $(\eta^2\text{-}O_2)_2TiO$, which possesses a $^3A''$ ground state and a nonplanar C_s geometry.

Introduction

The electronic and geometric structures of simple titanium oxide molecules and small clusters have been the subject of numerous experimental and theoretical studies.[1−25] Among the TiO_x series, the titanium monoxide and dioxide molecules are the most widely investigated candidates both in the gas phase and in solid matrixes,[1−12] and a number of theoretical calculations were performed on the structure and bonding of these simple diatomic and triatomic systems and their clusters.[13−25] Compared with the rich investigations on titanium monoxide and dioxide, few studies have been carried out on the TiO_x species with x higher than two. As for the TiO_3 species, Chertihin and Andrews assigned a 972.1 cm^{-1} absorption to the end-on bonded OTiOO complex in the reaction of laser-ablated titanium atoms with dioxygen in solid argon.[9] Wu and Wang performed an anion photoelectron spectroscopic study on TiO_x with $x = 1-3$. The neutral TiO_3 molecule was proposed to contain a peroxide unit.[10] Theoretical calculations indicate that the ground state of TiO_3 possesses a nonplanar C_s symmetry with the peroxo O_2 unit bound to TiO in a side-on fashion.[18,19,21a] Studies on the next member in the TiO_x series, TiO_4, are mainly limited to the corresponding tetrahedral TiO_4^{4-} anion.[26−28] Recently, two interconvertible oxo-superoxo−titanium-ozonide complexes with TiO_6 stoichiometry in solid argon were prepared and characterized in this laboratory.[29]

In this paper, we provide a joint matrix isolation infrared spectroscopic and theoretical investigation on the formation and characterization of the TiO_3 and TiO_5 molecules. These titanium oxide species with odd number of oxygen atoms were formed via the reactions of laser-evaporated titanium monoxide and O_2 in solid argon. The TiO_3 molecule was characterized to be a side-on bonded peroxo titanium monoxide complex, whereas TiO_5 was characterized to be a side-on bonded disuperoxotitanium monoxide complex.

Experimental and Computational Methods

The experimental setup for pulsed laser-evaporation and matrix isolation infrared spectroscopic investigation has been described in detail previously.[30] Briefly, the 1064 nm fundamental of a Nd:YAG laser (Continuum, Minilite II, 10 Hz repetition rate and 6 ns pulse width) was focused onto a rotating titanium dioxide or metallic titanium target through a hole in a CsI window cooled normally to 6 K by means of a closed-cycle helium refrigerator (ARS, 202N). The laser-evaporated species were codeposited with O_2/Ar mixtures onto the CsI window. In general, matrix samples were deposited for 1 h at a rate of approximately 4 mmol/h. The O_2/Ar mixtures were prepared in a stainless steel vacuum line by using standard manometric technique. Isotopic $^{18}O_2$ (ISOTEC, 99%) was used without further purification. The infrared absorption spectra of the resulting samples were recorded on a Bruker IFS 66V spectrometer at 0.5 cm^{-1} resolution between 4000 and 450 cm^{-1} by using a liquid nitrogen cooled HgCdTe (MCT) detector. Samples were annealed to different temperatures and cooled back to 6 K for spectral acquisition.

Quantum chemical calculations were performed by using the Gaussian 03 program.[31] The three-parameter hybrid functional according to Becke with additional correlation corrections due to Lee, Yang, and Parr (B3LYP) was utilized.[32] The 6-311+G(d) basis set was used for the O atom, and the all electron basis set of Wachters−Hay as modified by Gaussian was used for the Ti atom.[33] The geometries were fully optimized; the harmonic vibrational frequencies were calculated, and zero-point vibrational energies were derived.

Results and Discussions

Infrared Spectra. A series of experiments were performed by using a bulk titanium dioxide target with different O_2 concentrations. Laser ablation of the TiO_2 target under controlled laser energy (approximately 3 mJ/pulse) followed by co-condensation with pure argon formed TiO and TiO_2 as the major products.[9] The Ti_2O_4 cluster absorptions were produced on sample annealing at the expense of TiO_2.[34] Distinct new product absorptions were observed when O_2/Ar was used as reagent gas. The infrared spectra in selected regions from codeposition of laser evaporated titanium oxide species with 0.5% O_2 in argon are shown in Figure 1, and the product absorptions are listed in Table 1. Besides the TiO, TiO_2, and Ti_2O_4 absorptions, two groups of new absorptions were evolved upon sample annealing as shown in Figure 1, traces b and c. The first group includes four absorptions centered at 971.9, 863.3, 624.8, and 611.1 cm^{-1},

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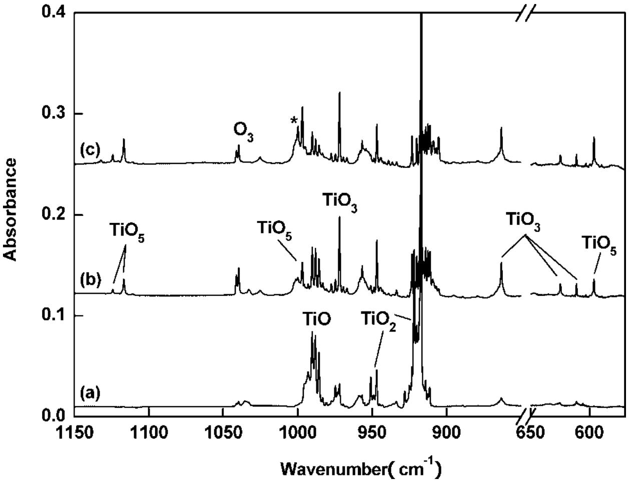

Figure 1. Infrared spectra in the 1150−850 and 650−570 cm^{-1} regions from codeposition of laser-evaporated titanium oxides with 0.5% O_2 in argon. (a) 1 h of sample deposition at 6 K, (b) after 25 K annealing, and (c) after 35 K annealing. The asterisk denotes the absorption of TiO_6.

which were produced upon 25 K annealing (Figure 1, trace b) at the expense of the TiO absorptions. The second group involves four absorptions with band positions at 1124.1, 1116.6, 996.8, and 596.4 cm^{-1}. This group of absorptions also appeared on 25 K annealing and doubled upon 35 K annealing during which the first group of absorptions decreased slightly. In addition, the absorptions due to TiO_6 and O_3 were also produced on sample annealing.[29,35]

To help the product assignments, experiments were repeated with the isotopic labeled $^{18}O_2$ sample and the $^{16}O_2 + ^{18}O_2$ and $^{16}O_2 + ^{16}O^{18}O + ^{18}O_2$ mixtures. The spectra in selected regions from codeposition of laser-evaporated titanium oxides with different isotopic samples taken after 1 h of sample deposition followed by 35 K annealing are shown in Figures 2 and 3, respectively. The new product absorptions are shifted and splitted as listed in Table 1.

Complementary experiment on the reaction of laser-evaporated titanium atoms and 0.5% dioxygen in argon was also performed with a titanium metal target. The TiO_2, Ti_2O_4, and TiO_6 absorptions dominate the spectrum, but the TiO absorption is weak. The new 971.9, 863.3, 624.8, 611.1, 1124.1, 1116.6, 996.8, and 596.4 cm^{-1} absorptions were also produced on sample annealing, but their IR intensities are much weaker than those in the experiment with bulk TiO_2 target. Similar experiment with the Ti target was done by using the $^{18}O_2$/Ar sample to get the pure O-18 counterparts of the newly observed absorptions (Table 1).

TiO_3. The 971.9, 863.3, 624.8, and 611.1 cm^{-1} absorptions are due to different vibrational modes of the same species based on their behavior upon annealing at different experiments. These absorptions depend strongly on the TiO absorption, which led us to propose that these absorptions are due to a reaction product of TiO. The 971.9 cm^{-1} absorption was observed in the previous experiment on the reaction of laser-ablated titanium atom with dioxygen and was assigned to the Ti=O stretch vibration of an end-on bonded OTi-OO complex.[9] The observation of three additional absorptions helps us to reassign these absorptions to a side-on bonded titanium-monoxide−dioxygen complex. The 971.9 cm^{-1} absorption is about 20 cm^{-1} red-shifted from that of diatomic TiO. It shifted to 931.7 cm^{-1} with Ti + $^{18}O_2$. The band position and O-18 isotopic shift indicates that this absorption is due to a terminal Ti=O stretch mode of a titanium monoxide complex. The band position is quite close to those of previously characterized TiO containing species.[29,34,36,37] The natural titanium isotopic splittings on this mode can clearly be resolved, which proves that only one titanium atom is present in this species. The spectra from the experiments using $^{16}O_2 + ^{18}O_2$ and $^{16}O_2 + ^{16}O^{18}O + ^{18}O_2$ mixtures with bulk titanium dioxide target revealed that only one TiO fragment is involved in this mode (Figure 2, traces c and d). The next absorption lies at 863.3 cm^{-1} with the pure ^{18}O counterpart at 819.9 cm^{-1}. The spectral feature in the experiments with $^{16}O_2 + ^{16}O^{18}O + ^{18}O_2$ mixture implies that two equivalent oxygen atoms are involved in this mode. The $^{16}O/^{18}O$ isotopic ratio for this vibration (1.0529) suggests that this is not a pure normal O−O stretching mode; it may be coupled with the Ti=O stretch vibration. The 624.8 and 611.1 cm^{-1} absorptions are attributed to the Ti−O_2 vibrations.

Both the $(\eta^2\text{-}^{18}O_2)Ti^{16}O$ and $(\eta^2\text{-}^{16}O^{18}O)Ti^{18}O$ absorptions were observed in the spectrum with $^{18}O_2$/Ar and normal titanium dioxide target (Figure 2, trace b). This indicates that the oxygen atoms of the peroxo ligand can be interconverted with the oxygen atom of the monoxide subunit during the association reaction process.

The assignment of the $(\eta^2\text{-}O_2)TiO$ complex is strongly supported by density functional calculations. The DFT/B3LYP calculations revealed that the most stable structure of TiO_3 is the side-on bonded $(\eta^2\text{-}O_2)TiO$ complex. The end-on bonded OTi-OO isomer was predicted to be less stable than the side-on bonded structure by about 44.8 kcal/mol. The $(\eta^2\text{-}O_2)TiO$ complex possesses a singlet ground state with a nonplanar C_s symmetry, in which the terminal oxygen atom bends out of the $Ti(O_2)$ plane (Figure 4), in agreement with previous theoretical predictions.[18,19,21a] The four experimentally observed modes were computed at 1038.4, 909.5, 636.8, and 636.6 cm^{-1} with 309/124/35/36 km/mol IR intensities (Table 2). As listed in Table 3, the calculated isotopic frequency ratios are also in very good agreement with the experimental values.

The O−O bond length of $(\eta^2\text{-}O_2)TiO$ was calculated to be 1.471 Å. Although the O−O and Ti=O vibrations are coupled, the calculated O−O bond length implies that $(\eta^2\text{-}O_2)TiO$ is a peroxo complex of titanium monoxide.[38] It can be regarded as a titanium monoxide dication coordinated by an O_2^{2-} dianion, $[(O_2)^{2-}(TiO)^{2+}]$. The titanium center is in its formal +4 oxidation state. Similar transition metal peroxide complexes have been prepared and characterized in this laboratory.[39]

Recent experimental and theoretical investigations suggest that the titanium peroxide species is an important intermediate in the process of O_2 adsorption and photoreduction on TiO_2 surface.[40,41] In the experiments using multiple internal reflection infrared spectroscopic (MIRIR) technique, Nakamura et al. assigned an absorption at 943 cm^{-1} to the surface adsorbed peroxide species, $Ti(O_2)$, which can further be transferred to the TiOOH hydroperoxo species via capture of H^+ cations in aqueous solution.[40] The adsorbed peroxo dianion was rationalized to be located on a 5-fold coordinated surface Ti^{4+} cation.[41] The O−O stretch frequency of the isolated $(\eta^2\text{-}O_2)TiO$ complex is about 80 cm^{-1} lower than that of the surface adsorbed peroxo species, whereas the predicted O−O bond length for the surface adsorbed O_2^{2-} dianion of 1.46 Å,[41] is only slightly shorter than that of $(\eta^2\text{-}O_2)TiO$ (1.471 Å). The electron transfer from TiO to O_2 in forming the $(\eta^2\text{-}O_2)TiO$ complex is in accord with the mechanism of electron capture by adsorbed dioxygen molecule on metal oxide surface during photocatalytic process.

TABLE 1: Infrared Absorptions (cm^{-1}) from Co-Deposition of Laser-Evaporated TiO with O_2 in Solid Argon

$^{16}O_2$	$^{18}O_2$	$^{16}O_2 + {}^{18}O_2$	$^{16}O_2 + {}^{16}O^{18}O + {}^{18}O_2$	$^{18}O_2$[a]	assignment
977.5					$(\eta^2\text{-}O_2)^{46}TiO$
974.6					$(\eta^2\text{-}O_2)^{47}TiO$
971.9	971.7, 931.8	971.9, 931.8	971.9, 931.9	931.7	$(\eta^2\text{-}O_2)^{48}TiO$ Ti═O str
969.3					$(\eta^2\text{-}O_2)^{49}TiO$
966.9					$(\eta^2\text{-}O_2)^{50}TiO$
863.3	842.0, 820.4	863.3, 842.0, 820.4	863.3, 842.8, 820.4	819.9	$(\eta^2\text{-}O_2)TiO$ O−O str
624.8	611.5, 594.5	624.8, ...,[b] 594.5	624.8, ...,[b] 594.5	594.4	$(\eta^2\text{-}O_2)TiO$ asym Ti−O_2 str
611.1	595.9, 586.7	611.1, ...,[b] 586.7	611.1,[b] 586.7	586.1	$(\eta^2\text{-}O_2)TiO$ sym Ti−O_2 str
1124.1	1089.6, 1060.9	1124.1, 1120.2, 1116.6	1124.1, 1120.2, 1116.6	1061.0	$(\eta^2\text{-}O_2)_2TiO$ sym O−O str
1116.6	1058.0, 1054.4	1089.6, 1060.9, 1058.3, 1054.4	1093.2, 1089.6, 1086.1, 1060.9, 1058.3, 1054.4	1054.4	$(\eta^2\text{-}O_2)_2TiO$ asym O−O str
996.8	996.8, 955.5	996.8, 955.5	996.8, 955.5	955.5	$(\eta^2\text{-}O_2)_2TiO$ Ti═O str
596.4	584.0, 581.2	596.2, 589.5, 584.1, 581.3	594.3, 591.8, 589.6, 584.4, 581.4	580.8	$(\eta^2\text{-}O_2)_2TiO$ asym Ti-$(O_2)_2$ str

[a] Absorptions observed in the reaction of Ti and $^{18}O_2$. [b] Absorptions unresolved because of band overlap.

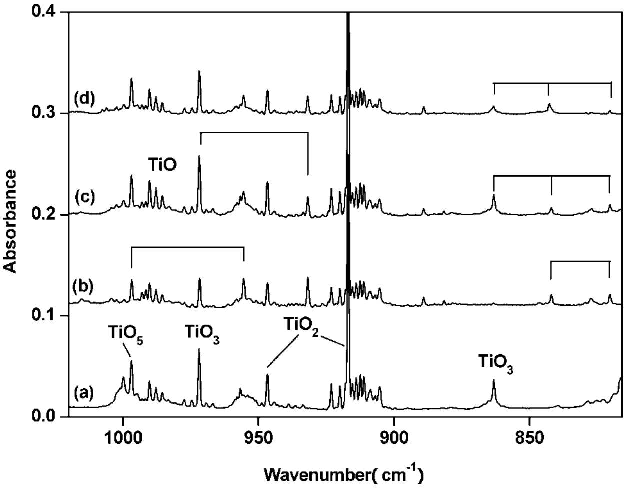

Figure 2. Infrared spectra in the 1020−816 cm^{-1} region from codeposition of laser-evaporated titanium oxides with isotopic-labeled dioxygen in excess argon. Spectra were taken after 1 h of sample deposition followed by 35 K annealing. (a) 0.5% $^{16}O_2$, (b) 0.5% $^{18}O_2$, (c) 0.2% $^{16}O_2$ + 0.2% $^{18}O_2$, and (d) 0.15% $^{16}O_2$ + 0.3% $^{16}O^{18}O$ + 0.15% $^{18}O_2$.

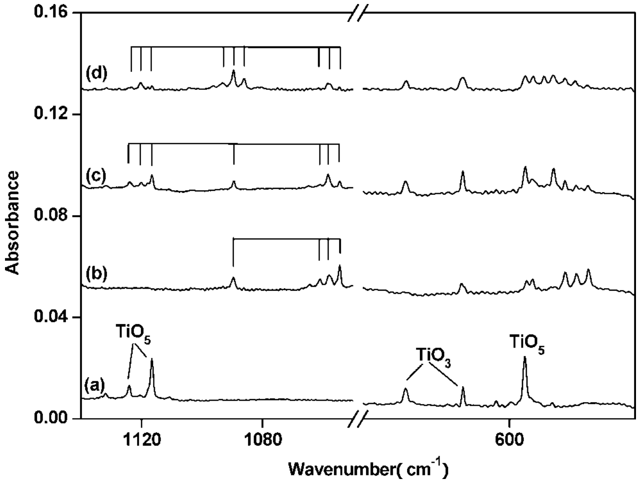

Figure 3. Infrared spectra in the 1140−1050 and 635−570 cm^{-1} regions from codeposition of laser-evaporated titanium oxides with isotopic-labeled dioxygen in excess argon. Spectra were taken after 1 h of sample deposition followed by 35 K annealing. (a) 0.5% $^{16}O_2$, (b) 0.5% $^{18}O_2$, (c) 0.2% $^{16}O_2$ + 0.2% $^{18}O_2$, and (d) 0.15% $^{16}O_2$ + 0.3% $^{16}O^{18}O$ + 0.15% $^{18}O_2$.

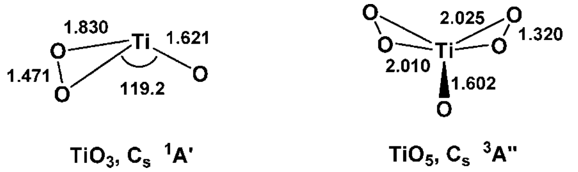

Figure 4. Optimized structures (bond lengths in angstrom and bond angles in degree) of the observed products.

TiO_5. The 1124.1, 1116.6, 996.8, and 596.4 cm^{-1} absorptions increased together upon sample annealing after the $(\eta^2\text{-}O_2)TiO$ absorptions. Experiments with different O_2 concentrations revealed that these absorptions are favored with higher O_2 content relative to the TiO_3 absorptions, which suggests that the absorber should involve more oxygen than that in TiO_3. The 996.8 cm^{-1} absorption is the strongest one in this group, which shifted to 955.5 cm^{-1} with $^{18}O_2$. This absorption is attributed to a terminal Ti═O stretch mode based upon its band position and oxygen isotopic shift following the example of $(\eta^2\text{-}O_2)TiO$. The 1124.1 and 1116.6 cm^{-1} absorptions exhibit similar isotopic ratios which are characteristic of O−O stretch vibrations. In addition to the absorptions observed in the experiments with $^{16}O_2$ and $^{18}O_2$ separately, two intermediate absorptions at 1120.2 and 1058.3 cm^{-1} were observed in the experiment using a mixed $^{16}O_2 + {}^{18}O_2$ sample (Figure 3, trace c). This experimental observation demonstrates that the 1124.1 and 1116.6 cm^{-1} absorptions are due to the symmetric and antisymmetric O−O stretch vibrations originating from a species involving two equivalent O_2 subunits. On the basis of the experimental observations, we assign the 1124.1, 1116.6, 996.8, and 596.4 cm^{-1} absorptions to the $(\eta^2\text{-}O_2)_2TiO$ complex. The 596.4 cm^{-1} absorption is due to a Ti-$(O_2)_2$ stretch vibration.

To further support the assignment, theoretical calculations were carried out on this TiO_5 species. As shown in Figure 4, the most stable configuration for the $(\eta^2\text{-}O_2)_2TiO$ complex was found to have a nonplanar C_s geometry with a $^3A''$ ground state. The two O_2 groups roughly form a plane, which is perpendicular to the TiO fragment. Compared with the $(\eta^2\text{-}O_2)TiO$ complex, the terminal TiO bond length of the $(\eta^2\text{-}O_2)_2TiO$ complex is shortened by 0.019 Å upon coordination of a second O_2 molecule. The two O−O bonds exhibit the same bond length which was calculated to be 1.320 Å, much shorter than that of the $(\eta^2\text{-}O_2)TiO$ complex. The O−O bond length of $(\eta^2\text{-}O_2)_2TiO$ is very close to those of the recently characterized transition metal superoxide complexes.[39,42] Therefore, the $(\eta^2\text{-}O_2)_2TiO$ complex can be described as a disuperoxo titanium monoxide complex, $[(O_2^-)_2(TiO)^{2+}]$, which also stratifies the +4 oxidation state of Ti. Consistent with this notion, the $(\eta^2\text{-}O_2)_2TiO$ complex has a triplet ground state with the two unpaired electrons located on the two O_2 fragments (1.06 e each). On the basis of the calculation results, the four experimentally observed vibrational modes for the $(\eta^2\text{-}O_2)_2TiO$ complex were predicted at 1198.4,

TABLE 2: DFT/B3LYP Calculated Total Energies[a], Frequencies (cm^{-1}), and Intensities (km/mol) of the Products

molecule	energy	frequency (intensity)
(η^2-O_2)TiO ($^1A'$, C_s)	−1075.188968	1038.4 (309) 909.5 (124) 636.8 (35) 636.6 (36) 234.3 (36) 205.6 (21)
(η^2-O_2)$_2$TiO ($^3A''$, C_s)	−1225.620590	1198.4 (16) 1184.8 (78) 1068.8 (244) 587.1 (112) 499.0 (10) 453.4 (2) 453.3 (20) 222.2 (19) 219.8 (3) 159.0 (0) 137.7 (4) 96.7(30)

[a] In Hartree, after zero point energy corrections.

TABLE 3: Comparison Between the Observed and Calculated Vibrational Frequencies (cm^{-1}) and Isotopic Frequency Ratios of the Product Molecules

		freq		$^{16}O/^{18}O$[a]	
molecule	mode	calcd	obsd	calcd	obsd
(η^2-O_2)TiO ($^1A'$, C_s)					
	Ti═O str. (a′)	1038.4	971.9	1.0438	1.0431
	O−O str. (a′)	909.5	863.3	1.0540	1.0529
	asym Ti−O_2 str. (a”)	636.8	624.8	1.0517	1.0511
	sym Ti−O_2 str. (a′)	636.6	611.1	1.0433	1.0427
(η^2-O_2)$_2$TiO ($^3A''$, C_s)					
	sym O−O str. (a′)	1198.4	1124.1	1.0607	1.0595
	asym O−O str. (a”)	1184.8	1116.6	1.0606	1.0590
	Ti═O str. (a′)	1068.8	996.8	1.0439	1.0432
	asym Ti-(O_2)$_2$ str. (a”)	587.1	596.4	1.0257	1.0269

[a] Oxygen-18 refers to $Ti^{18}O_3$ and $Ti^{18}O_5$.

1184.8, 1068.8, and 587.1 cm^{-1} with the calculated isotopic $^{16}O/^{18}O$ ratios in good agreement with the experimental values (Table 3). These four modes were predicted to have the largest IR intensities; all the other modes are either out of the spectral range or have very low IR intensities (Table 2).

Reaction Mechanism. Laser evaporation of bulk titanium dioxide produces substantial amount of titanium monoxide molecules, which are trapped and isolated in solid argon. When the as-deposited sample containing TiO and O_2 was annealed, the reactants can diffuse and react to form the (η^2-O_2)TiO and (η^2-O_2)$_2$TiO complexes. According to the DFT/B3LYP calculations, the formation of the (η^2-O_2)TiO complex from the ground state of TiO and O_2 is exothermic by 80.7 kcal/mol (reaction 1). The formation of the (η^2-O_2)TiO complex upon annealing indicates that reaction 1 requires negligible activation energy.

$$\mathrm{TiO}(^3\Delta) + \mathrm{O_2}\left(^3\sum\nolimits_g^-\right) \rightarrow (\eta^2\text{-}\mathrm{O_2})\mathrm{TiO}(^1A') \qquad \Delta E = -80.7\ \mathrm{kcal/mol} \quad (1)$$

The (η^2-O_2)$_2$TiO complex absorptions increased after the (η^2-O_2)TiO absorptions. This suggests that the (η^2-O_2)TiO complex can further react with another molecular oxygen to give the (η^2-O_2)$_2$TiO complex, reaction 2. The spontaneous formation of the (η^2-O_2)$_2$TiO complex upon sample annealing implies that reaction 2 is also a barrierless reaction, which was predicted to be exothermic by 40.7 kcal/mol.

$$(\eta^2\text{-}\mathrm{O_2})\mathrm{TiO}(^1A') + \mathrm{O_2}\left(^3\sum\nolimits_g^-\right) \rightarrow (\eta^2\text{-}\mathrm{O_2})_2\mathrm{TiO}(^3A'') \qquad \Delta E = -40.7\ \mathrm{kcal/mol} \quad (2)$$

The photoreduction of molecular oxygen on titanium oxide surface was proposed to proceed from the initial formation of a surface superoxo species TiOO complex, followed by its reduction to produce a surface peroxo $Ti(O_2)^{2-}$ species with a double negative charge.[40,41] The above characterized (η^2-O_2)TiO and (η^2-O_2)$_2$TiO complexes may serve as the simplest model in understanding the adsorbed species on titanium oxide surface. However, the Ti site on the titanium oxide surface is 5-fold coordinated; it can only adsorb one O_2 molecule in forming the charge transferred superoxo and peroxo species. The TiO molecule can be regarded as only one-fold coordinated; therefore, it can either coordinate one O_2 molecule in forming the peroxo complex or coordinate two O_2 molecules to give the disuperoxo complex to satisfy the +4 oxidation state of Ti.

With the two complexes characterized here, a series of complexes between titanium monoxide and small molecule ligands have been reported.[37,43,44] The (CH_4)TiO complex was found to be very weakly bound with a binding energy of only about 1.1 kcal/mol.[37] Different from the spherical methane molecule, the water molecule can serve as a σ donor owing to the existence of two pairs of lone-pair electrons. Hence, the TiO molecule was able to coordinate with water molecule to form the (H_2O)TiO complex with a predicted binding energy of 16.1 kcal/mol, much higher than that of (CH_4)TiO.[43] The (C_2H_2)TiO and (OC)TiO complexes were predicted to have large binding energies of 38.3[44a] and 23 kcal/mol (DFT/BP86 method).[45] This may be attributed to the existing of both σ donation and π back-donation interactions between TiO and CO or C_2H_2. The above-characterized (η^2-O_2)TiO and (η^2-O_2)$_2$TiO charge transfer complexes have the largest binding energies in this set (80.7 kcal/mol for the former and 60.7 kcal/mol per O_2 for the latter).

Conclusions

The reaction of titanium monoxide molecules and O_2 was investigated by using matrix isolation infrared spectroscopy and theoretical calculations. Laser evaporation of bulk titanium dioxide produces substantial amount of titanium monoxide molecules, which are trapped and isolated in solid argon. When the as-deposited sample containing TiO and O_2 was annealed, the reactants can diffuse and react to form the (η^2-O_2)TiO complex, which is characterized to be a peroxo titanium monoxide complex, $(O_2)^{2-}(TiO)^{2+}$, with a nonplanar C_s symmetry and a $^1A'$ ground state. The (η^2-O_2)TiO complex is able to further react with another molecular oxygen to give the (η^2-O_2)$_2$TiO complex, which can be described as a disuperoxo titanium monoxide complex, $(O_2^-)_2(TiO)^{2+}$. The (η^2-O_2)$_2$TiO complex was predicted to possess a $^3A''$ ground state and a nonplanar C_s geometry. These simple superoxo and peroxo titanium monoxide complexes may serve as simple model in understanding the adsorbed species on titanium oxide surface.

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References and Notes

(1) Weltner, W., Jr.; McLeod, D., Jr. *J. Phys. Chem.* **1965**, *69*, 3488.

(2) Powell, D.; Brittain, R.; Vala, M. *Chem. Phys.* **1981**, *58*, 355.

(3) Dyke, J. M.; Gravenor, B. W.; Josland, G. D.; Lewis, R. A.; Morris, A. *Mol. Phys.* **1984**, *53*, 465.

(4) (a) Steimle, T. C.; Shirley, J. E.; Jung, K. Y.; Russon, L. R.; Scurlock, C. T. *J. Mol. Spectrosc.* **1990**, *144*, 27. (b) Steimle, T. C.; Shirley, J. E. *J. Chem. Phys.* **1989**, *91*, 8000.

(5) (a) Kobayashi, K.; Hall, G. E.; Muckerman, J. T.; Sears, T. J.; Merer, A. J. *J. Mol. Spectrosc.* **2002**, *212*, 133. (b) Barnes, M.; Merer, A. J.; Metha, G. F. *J. Mol. Spectrosc.* **1997**, *181*, 180. (c) Merer, A. J. *Annu. Rev. Phys. Chem.* **1989**, *40*, 407.

(6) Kaledin, L. A.; McCord, J. E.; Heaven, M. C. *J. Mol. Spectrosc.* **1995**, *173*, 499.

(7) Loock, H.; Simard, B.; Wallin, S.; Linton, C. *J. Chem. Phys.* **1998**, *109*, 8980.

(8) McIntyre, N. S.; Thompson, K. R.; Weltner, W., Jr. *J. Phys. Chem.* **1971**, *75*, 3243.

(9) Chertihin, G. V.; Andrews, L. *J. Phys. Chem.* **1995**, *99*, 6356.

(10) Wu, H. B.; Wang, L. S. *J. Chem. Phys.* **1997**, *107*, 8221.

(11) Zhai, H. J.; Wang, L. S. *J. Am. Chem. Soc.* **2007**, *129*, 3022.

(12) Bruenken, S.; Mueller, H. S. P.; Menten, K. M.; McCarthy, M. C.; Thaddeus, P. *Astrophys. J.* **2008**, *676*, 1367.

(13) (a) Gutsev, G. L.; Andrews, L.; Bauschlicher, C. W., Jr. *Theor. Chem. Acc.* **2003**, *109*, 298. (b) Gutsev, G. L.; Rao, B. K.; Jena, P. *J. Phys. Chem. A* **2000**, *104*, 5374. (c) Bauschlicher, C. W., Jr.; Maitre, P. *Theor. Chim. Acta* **1995**, *90*, 189. (d) Bauschlicher, C. W., Jr.; Langhoff, S. R.; Komornicki, A. *Theor. Chim. Acta* **1990**, *77*, 263. (e) Bauschlicher, C. W.; Bagus, P. S.; Nelin, C. J. *Chem. Phys. Lett.* **1983**, *101*, 229.

(14) Dai, B.; Deng, K. M.; Yang, J. L.; Zhu, Q. S. *J. Chem. Phys.* **2003**, *118*, 9608.

(15) Ramana, M. V.; Phillips, D. H. *J. Chem. Phys.* **1988**, *88*, 2637.

(16) Hagfeldt, A.; Bergström, R.; Siegbahn, H. O. G.; Lunell, S. *J. Phys. Chem.* **1993**, *97*, 12725.

(17) Rosi, M.; Bauschlicher, C. W.; Chertihin, G. V.; Andrews, L. *Theor. Chem. Acc.* **1998**, *99*, 106.

(18) Walsh, M. B.; King, R. A.; Schaefer, H. F., III *J. Chem. Phys.* **1999**, *110*, 5224.

(19) Jeong, K. S.; Chang, Ch,.; Sedlmayr, E.; Sülzle, D. *J. Phys. B* **2000**, *33*, 3417.

(20) Gutsev, G. L.; Rao, B. K.; Jena, P. *J. Phys. Chem. A* **2000**, *104*, 11961.

(21) (a) Albaret, T.; Finocchi, F.; Noguera, C. *J. Chem. Phys.* **2000**, *113*, 2238. (b) Albaret, T.; Finocchi, F.; Noguera, C. *Appl. Surf. Sci.* **1999**, *144*, 672.

(22) Qu, Z. W.; Kroes, G. J. *J. Phys. Chem. B* **2006**, *110*, 8998.

(23) (a) Woodley, S. M.; Hamad, S.; Mejias, J. A.; Catlow, C. R. A. *J. Mater. Chem.* **2006**, *16*, 1927. (b) Hamad, S.; Catlow, C. R. A.; Woodley, S. M.; Lago, S.; Mejías, J. A. *J. Phys. Chem. B* **2005**, *109*, 15741.

(24) Grein, F. *J. Chem. Phys.* **2007**, *126*, 034313.

(25) Uzunova, E. L.; Mikosch, H.; Nikolov, G. St. *J. Chem. Phys.* **2008**, *128*, 094307.

(26) Bridgeman, A. J.; Cavigliasso, G. *Polyhedron* **2001**, *20*, 2269.

(27) Kun, K.; Brown, I. D. *Acta Crystallogr., Sect. B* **1973**, *29*, 2009.

(28) Gonzalez-Vilchez, F.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1972**, 1416.

(29) Gong, Y.; Zhou, M. F.; Tian, S. X.; Yang, J. L. *J. Phys. Chem. A* **2007**, *111*, 6127.

(30) Wang, G. J.; Zhou, M. F. *Int. Rev. Phys. Chem.* **2008**, *27*, 1.

(31) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.05; Gaussian, Inc.: Wallingford, CT, 2004.

(32) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(33) (a) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639. (b) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(34) Gong, Y.; Zhang, Q. Q.; Zhou, M. F. *J. Phys. Chem. A* **2007**, *111*, 3534.

(35) Andrews, L.; Spiker, R. C., Jr. *J. Phys. Chem.* **1972**, *76*, 3208.

(36) (a) Zhou, M. F.; Zhang, L. N.; Dong, J.; Qin, Q. Z. *J. Am. Chem. Soc.* **2000**, *122*, 10680. (b) Miao, L.; Dong, J.; Yu, L.; Zhou, M. F. *J. Phys. Chem. A* **2003**, *107*, 1935.

(37) Wang, G. J.; Gong, Y.; Chen, M. H.; Zhou, M. F. *J. Am. Chem. Soc.* **2006**, *128*, 5974.

(38) Cramer, C. J.; Tolman, W. B.; Theopold, K. H.; Rheingold, A. L. *Proc. Natl. Acad. Sci. U. S. A.* **2003**, *100*, 3635.

(39) (a) Gong, Y.; Zhou, M. F. *J. Phys. Chem. A* **2007**, *111*, 8973. (b) Gong, Y.; Zhou, M. F.; Andrews, L. *J. Phys. Chem. A* **2007**, *111*, 12001. (c) Gong, Y.; Wang, G. J.; Zhou, M. F. *J. Phys. Chem. A* **2008**, *112*, 4936.

(40) Nakamura, R.; Imanishi, A.; Murakoshi, K.; Nakato, Y. *J. Am. Chem. Soc.* **2003**, *125*, 7443.

(41) (a) Mattioli, G.; Filippone, F.; Bonapasta, A. A. *J. Am. Chem. Soc.* **2006**, *128*, 13772. (b) Filippone, F.; Mattioli, G.; Bonapasta, A. A. *Catal. Today* **2007**, *129*, 169.

(42) Gong, Y.; Ding, C. F.; Zhou, M. F. *J. Phys. Chem. A* **2007**, *111*, 11572.

(43) Shao, L. M.; Zhang, L. N.; Chen, M. H.; Lu, H.; Zhou, M. F. *Chem. Phys. Lett.* **2001**, *343*, 178.

(44) (a) Wang, G. J.; Chen, M. H.; Zhao, Y. Y.; Zhou, M. F. *Chem. Phys.* **2006**, *322*, 354. (b) Zhou, M. F.; Andrews, L. *J. Phys. Chem. A* **1999**, *103*, 2066.

(45) Pápai, I.; Mascetti, J.; Fournier, R. *J. Phys. Chem. A* **1997**, *101*, 4465.

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