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Infrared Spectroscopy and Density Functional Theory Investigations of the Reactivity of Titanium Atoms with Carbon Monoxide and Water Isolated in Solid Argon: Sequential Evolution from Triplet to Singlet State

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Abstract

Thermally evaporated titanium atoms react with carbon monoxide and water in solid argon at 12 K to produce the HTiOH-CO and HTiOH-(CO)₂ molecules which ~~are~~ were characterized using infrared spectroscopy on the basis of CO, Ti, and water concentration variations and of isotopic substitutions. The insertion product, HTiOH, resulting from the reaction of a titanium atom with a water molecule reacts with CO spontaneously to give the HTiOH-CO molecule which in turn reacts with a second CO molecule to give HTiOH-(CO)₂. The Density Functional Theory (DFT) calculations have been carried out to elucidate the geometrical and electronic structures and support the spectral assignments. The topological analysis of the charge density within the experimentally observed molecules allowed us to rationalize the coordination sphere as well as the electron pairing on the titanium center.

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INTRODUCTION

The water gas shift reaction, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ is frequently applied in the chemical process industry for H_2 production¹ and it also plays a secondary role in many proposed future technologies for energy conversion. Many experimental²⁻⁴ and theoretical⁵ studies have been performed to elucidate the reaction mechanisms and investigate the catalytic active species.

Reactions of laser-ablated transition metals with two ligands have been investigated in solid argon or neon. Andrews has studied the reactions of ruthenium atoms with $\text{CO} + \text{H}_2$ mixtures in which $\text{H}_2\text{Ru}(\text{CO})_x$ ($x=1-4$) molecules were formed and identified in solid argon⁶. A second investigation, carried out on the interaction of Mn, Fe, Co and Ni atoms with $\text{O}_2 + \text{H}_2$ mixtures, $\text{M}(\text{OH})_{1,2,3}$ molecules were characterized in solid argon⁷. In a study where metal atoms were reacted with $\text{N}_2 + \text{CO}$, Xu and co-workers identified NNMCO ($\text{M}=\text{Ta}, \text{Nb}$), $(\text{NN})_2\text{TaCO}$ and $\text{NNTa}(\text{CO})_2$ molecules in solid neon⁸, while copper atoms with $\text{CO} + \text{N}_2$ mixture in solid argon resulted in the formation of the NNCuCO and $(\text{NN})_2\text{CuCO}$ complexes⁹. The latter results show that the preadsorption of CO on Cu atoms promotes adsorption of N_2 . Additionally Xu has studied the interaction of Cu, Ag and Au atoms with O_2 and CO and different molecules have been characterized: $(\text{O}_2)\text{Cu}(\text{CO})_{1,2}$, $\text{OO}(\text{M})\text{CO}$ ($\text{M}=\text{Cu}, \text{Ag}$), OCAuO_2CO and OAuCO ¹⁰. Finally, Zhou has studied the interactions of water molecules with platinum dioxygen complex and dioxide molecule and three $\text{PtO}_2\text{-H}_2\text{O}$ complexes were identified¹¹. In another work, the reactions of early lanthanide metal atoms (Ce, Pr, and Nd) with carbon monoxide and nitric oxide have been investigated. The results show that the reactions proceed with the initial formation of a linear inserted NLnO molecules which subsequently reacts with CO to form the $\text{NLnO}(\text{CO})$ complexe¹².

Experimental and theoretical investigations have been carried out on the reactions of titanium atoms with water exclusively. Using infrared spectroscopy, Kauffman et al. showed that thermally evaporated Sc, Ti and V atoms in solid argon could react spontaneously with water molecules to form the insertion product HMOH ¹³. They have observed, without knowing it, the Ti-O stretching mode of the H_2TiO molecule, which they mistakenly assigned to the TiO molecule. Zhou and co-workers have studied the reactivity of laser evaporated Ti, V, Nb, Zr and Hf atoms with water in solid argon by infrared spectroscopy and with the help

of theoretical frequency calculations^{14,15}. Their findings show that the metals react spontaneously with water molecules to form insertion product HMOH and H₂M(OH)₂. In the case of the Ti atoms, the photolysis induces two reactional pathways for HTiOH: rearrangement to form H₂TiO isomer and H₂ elimination to form the monoxide, TiO.

The reactivity of titanium clusters with CO has received attention in the last decade. On one hand, when laser-ablated titanium atoms are codeposited with carbon monoxide, Ti(CO)_n (n=1-6)¹⁶, Ti₂(CO)_n (n=1,2), and Ti₃(CO)_n (n=1-3) molecules have been characterized in solid argon^{16,17} or neon¹⁸. On the other hand, when thermally evaporated Ti atoms react with CO, the TiCO molecule is not observed, but Ti₂CO and OTi₂C are observed in solid argon and neon¹⁹.

In this paper, we present the study of the reactivity of thermally evaporated titanium atoms with carbon monoxide and water in solid argon at 12 K. Infrared spectroscopy coupled with density functional calculations provide-evidences for the formation of two molecules HTiOH-CO and HTiOH-(CO)₂.

Experimental and Computational Details

The experimental setup for matrix isolation Fourier transform infrared (FTIR) spectroscopic investigation has been described in detail previously²⁰. Briefly, the samples were prepared by co-condensing Ti vapors and CO (1 to 4% CO in Ar) and H₂O (0.5% to 1%) mixtures in argon onto one of six flat, highly polished, Rh-plated copper mirrors maintained at 12 K using a closed cycle cryogenerator (model PT405, Cryomech, Syracuse, NY, USA) situated in a stainless-steel cell evacuated at a base pressure less than 5×10⁻⁷ mbar. A Ti-Mo filament (Goodfellow, 85% Ti) was heated at about 1500°C to generate Ti vapor. The metal's deposition rate was carefully monitored with the aid of a quartz microbalance and was typically of the order of 1–10 µg min⁻¹. High-purity argon (Prodair; 99.995%), carbon monoxide (Matheson; 99.5%), ¹³C¹⁶O (CEA, Saclay, France, 99% ¹³C¹⁶O including 9% ¹³C¹⁸O), ¹²C¹⁸O (MSD; 98% ¹⁸O) and H₂¹⁶O, H₂¹⁸O (98% ¹⁸O) and D₂¹⁸O (98.4% ¹⁸O) were used to prepare the CO–Ar and H₂O–Ar mixtures after removing condensable impurities with a liquid-N₂ trap.

In general, after 15-90 min of deposition, infrared spectra of the resulting sample were recorded at 0.1 cm⁻¹ resolution in the transmission–reflection mode between 4000 and 70 cm⁻¹ using a Bruker 120 FTIR

spectrometer and suitable combinations of KBr/Ge or Si/Mylar(6 μ m) beamsplitters with either liquid-N₂-cooled InSb or narrow-band HgCdTe photodiodes or a liquid-He-cooled Si-B bolometer, fitted with cooled bandpass filters. Bare mirror backgrounds were used as references in processing the sample spectra. Also, absorption spectra in the mid- and far infrared were collected on the same samples through either CsI or polyethylene windows mounted on a rotatable flange separating the interferometer vacuum (10⁻³ mbar) from the cryostatic cell (10⁻⁷ mbar). The spectra were subsequently subjected to baseline correction to compensate for infrared light scattering and interference patterns. The sample can be annealed in order to increase the abundance of aggregates.

Molecular geometries were optimized using the DFT B3LYP method with a correlation consistent basis set of triple-zeta quality (cc-pVTZ) for C, O and Ti atoms and the cc-pVTZ-PP basis set with extended relativistic pseudo-potentials for Ti obtained from the Basis Set Exchange (BSE) software and the EMSL Basis Set Library.²¹⁻²² All calculations have been performed with the Gaussian 09 quantum chemical package²³. Vibrational frequency analysis has been done within the harmonic approximation. The nature of chemical bonds between metal-ligand has been investigated using the QTAIM topological approach²⁴ with the AIMALL software²⁵.

EXPERIMENTAL RESULTS

Two samples were first prepared with Ti vapor: a first one with a CO/Ar concentration of 0.5% and a second with a H₂O/Ar concentration of 1% (spectra (a) and (b) in Figure 1). Some absorptions of products of Ti species with CO molecule were observed at 707.0, 754.4, and 769.8 cm⁻¹ and assigned to OTi₂C¹⁹, while two absorptions in the CO stretching region at 1866.7 and 1862.8 cm⁻¹ were assigned by Andrews¹⁶ to OTiCO and OTi(CO)₂ (Figure 1a). Other absorptions assigned by Zhou¹⁴ and Margrave¹³ to Ti species with water are dominant in the Ti-H and Ti-O stretching regions: peaks at 1538, 1549, and 699.6 cm⁻¹ assigned to HTiOH, at 1646.7 and 1010.8 cm⁻¹ assigned to H₂TiO¹⁴, and at 1666.0 and 1689.8 cm⁻¹ assigned to H₂Ti(OH)₂¹⁴ (Figure 1b). For a sample with Ti atoms and a CO+H₂O mixture, new bands were observed in O-H, C-O, Ti-H and Ti-O stretching regions at 3745.6, 2039.9, 1931.7, 1926.3, 1911.4, 1908.1 1577.4, 1549.4, 1543.8, 713.0, and 702.6 cm⁻¹ (Table 1). Other weak bands were observed, but no definitive

identification is possible. The band at 1595.5 cm^{-1} appears without the Ti vapor and has been previously assigned to the $(\text{CO})_2\text{-H}_2\text{O}$ complex²⁶. The new absorptions are indicated by arrows (except the bands at 3745.6 and 2039.9 cm^{-1}) in Figure 1. In order to attribute these bands to a specific species, experiments were done by performing several concentration studies and isotopic substitutions.

A series of experiments were performed using different Ti concentrations. When we increase the titanium flow rate by a factor of 2, with a constant $\text{CO}/\text{H}_2\text{O}/\text{Ar}$ concentration of 20/10/1000, we observed that the intensities of the new bands in **Figure 1** are multiplied by 2. We note the same intensity variation for both bands at 1866.7 and 1862.8 cm^{-1} which correspond to the species OTiCO and $\text{OTi}(\text{CO})_2$ ¹⁶ and this suggests that all the new bands correspond to species that contain one titanium atom (**Figure 1 and 2**).

Table 1. *Experimental vibrational frequencies and isotopic shifts (in cm^{-1}) for the observed molecules.*

$\text{H}_2\text{O} + \text{CO}$ isotopes					$\text{CO} + \text{H}_2\text{O}$ isotopes				Modes
$^{12}\text{C}^{16}\text{O}$	$^{13}\text{C}^{16}\text{O}$	$\Delta\nu$	$^{12}\text{C}^{18}\text{O}$	$\Delta\nu$	H_2^{18}O	$\Delta\nu$	D_2^{18}O	$\Delta\nu$	
3745.5	3745.4	0.1	3745.5	0	3733.5	12.0	-		ν_{OH}
2039.9 ^a	1994.0	45.9	1993.5	46.4	2039.8	0.1	2038.9	1.0	ν_{CO}
1931.7	1889.0	42.7	1887.5	44.2	1931.5	0.2	1929.1	2.6	ν_{CO}
1926.3	1883.7	42.6	1882.3	44.0	1926.1	0.2	1923.5	2.8	ν_{CO}
1911.4 ^b	1869.6	41.8	1865.3	46.1	1911.4	0.0	1910.9	0.5	ν_{CO}
1908.1	1866.5	41.6	1862.2	45.9	1908.4	0.0	1907.8	0.3	ν_{CO}
1577.4	1577.3	0.1	1577.3	0.1	1577.4	0.0	1138.4	439.0	$\nu_{\text{Ti-H}}$
1549.4	1549.1	0.3	1549.0	0.4	1549.3	0.1	1120.4	429.0	$\nu_{\text{Ti-H}}$
1543.8	1543.4	0.4	1543.3	0.5	1543.6	0.2	1116.9	426.9	$\nu_{\text{Ti-H}}$
713.0	-	-	-	-	-	-	-	-	$\nu_{\text{Ti-OH}}$
702.6	-	-	702.0	0.6	674.9	27.7	656.3	46.3	$\nu_{\text{Ti-OH}}$
389.2	386.0	3.2	385.6	3.6	387.3	1.9	352.7	36.5	n.a. ^c
358.7	353.3	5.4	356.8	1.9	358.1	0.6	-	-	n.a.
330.4	328.5	2.9	329.6	0.8	329.0	1.4	275.5	54.9	γ_{HOTiH}
312.2	-	-	-	-	312.2	0.0	281.5	30.7	n.a.

^a With the $^{12}\text{C}^{16}\text{O} + ^{12}\text{C}^{18}\text{O}$ mixture, a new band appears at 2020.7 cm^{-1}

^b With the $^{12}\text{C}^{16}\text{O} + ^{12}\text{C}^{18}\text{O}$ mixture, a new band appears at 1884.2 cm^{-1}

^c n.a.: not attributed bands

Figure 1. Infrared spectra in the (A) C-O, (B) Ti-H and (C) Ti-OH stretching regions of the $\text{Ti}+\text{CO}+\text{H}_2\text{O}$ reaction products at 12 K. $\text{Ti}/\text{CO}/\text{H}_2\text{O}/\text{Ar}=(a) 0.2/20/0/1000$, $(b) 0.2/0/10/1000$, and $(c) 0.2/20/10/1000$.

Figure 2. Infrared spectra in the (A) C-O and (B) Ti-H stretching regions of the Ti+CO+H₂O reaction products at 12 K. Ti/CO/H₂O/Ar=(a) 0.3/20/10/1000 and (b) 0.6/20/10/1000.

Experiments were done with CO concentrations of 1% and 2% and with a constant water (1%) and metal (600 ppm) concentration. The infrared spectra in the C-O and Ti-H regions are presented in **Figure 3**. The comparison between these two spectra shows that the intensities of the bands at 1931.7, 1926.3, 1866.8 (OTiCO), 1543.8, and 1549.4 cm⁻¹ increase by a factor of 2, but the bands at 1911.4, 1908.1, 1862.4 (OTi(CO)₂), and 1577.4 cm⁻¹ increase by a factor of 4. This suggests that the first group of bands corresponds to a species containing one CO molecule and the others to a species containing more than one CO (Table 1). Note that the bands observed at 713.0 and 702.6 cm⁻¹ in the Ti-O region correlate with those containing one CO. To correlate the band in the O-H stretching region at 3745.6 cm⁻¹ with the others, two samples were prepared at a lower water concentration (0.5%) but with two different CO concentrations, 2%

and 4% and with a constant Ti concentration of about 450 ppm. The band at 3745.6 cm^{-1} becomes more intense at higher concentration, which correlates with our observation for the band at 1577.4 cm^{-1} which has the same behavior (**Figure S1** in the Supporting Information).

Figure 3. Infrared spectra in the (A) C-O and (B) Ti-H stretching regions of the $\text{Ti}+\text{CO}+\text{H}_2\text{O}$ reaction products at 12 K. $\text{Ti/CO/H}_2\text{O/Ar}=(a)0.6/10/10/1000$ and $(b)0.6/20/10/1000$.

Complementary experiments were performed with 0.5 % and 1% water concentrations with a constant CO and Ti concentration (1% and 450 ppm, respectively). In the C-O and Ti-H stretching regions (**Figure 4**), when we increase the water concentration by a factor of 2, the intensities of the bands noted in **Figure 4** increase by a factor of 2. This suggests that the molecules corresponding to these bands contain one water molecule. We can conclude that the absorptions at 1926.3, 1931.7, 1543.7, 1549.4, 713.0 and 702.6 cm^{-1} can

be correlated together and attributed to the same species containing one CO and one H₂O molecule, and the other absorptions at 3745.6, 2039.9, 1911.4, 1908.1, and 1577.4 cm⁻¹ have the same behavior and belong to another species containing two CO molecules and one H₂O molecule.

Figure 4. Infrared spectra in the (A) C-O and (B) Ti-H stretching regions of the Ti+CO+H₂O reaction products at 12 K. Ti/CO/H₂O/Ar= (a)0.45/10/5/1000 and (b) 0.45/10/10/1000.

The bands for the species with one CO molecule present two different trapping sites (Table 1) and it was possible to discriminate them by annealing. After an annealing to 32 K, the intensities of the bands at 1926.3, 1543.8 and 702.6 cm⁻¹ remain almost unchanged but the intensities of the ones at 1931.7, 1549.4 and 713.0 cm⁻¹ increase by almost a factor of three (**Figure S2**). We can easily conclude that each doublet (Table 1) for each mode corresponds to two different trapping sites of the same species. The species with two CO

molecules has also two different trapping sites at 1911.4 and 1908.1 cm^{-1} , but in this case the first band is always the most intense, independently of the experimental conditions and the annealing temperature.

Accompanying these absorptions in the O-H, C-O, Ti-H, and Ti-OH stretching regions much weaker absorptions in the far infrared region have been observed. In order to correlate these bands with those observed in the mid-infrared region, several samples were prepared using different CO and H₂O concentrations. Figure 5a represents a spectrum with only a deposition of Ti and H₂O in Ar. For a sample with a CO/H₂O/Ar molar ratio of 10/10/1000, we observed four new absorptions at 389.2, 358.7, 330.4, and 312.2 cm^{-1} (**Figure 5b**). The other absorptions belong to species containing only Ti and water and are correlated with those observed in the Ti-H and Ti-O stretching regions. When we increase the CO concentration to 2%, these bands become more intense (**Figure 5c**), and with a higher CO concentration of 4% (**Figure 5d**), we observed that the intensity of the band at 330.4 cm^{-1} decreases by about 30%. We observe the same decrease for the species containing one CO molecule (Table 2). For the bands observed at 389.2, 358.7, and 312.2 cm^{-1} , the precise measurement of the intensities is impossible and they cannot be correlated with other observed bands.

Figure 5. Infrared spectra in the Far-infrared region of the (a) Ti+H₂O and (b), (c), (d) Ti+CO+H₂O reaction products at 12 K. Ti/Ar=0.45/1000 with CO/H₂O/Ar molar ratios of (a) 0/10/1000, (b) 10/10/1000, (c) 20/10/1000, and (d) 40/5/1000.

Isotopic substitutions were carried out using $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$, $\text{CO}+^{12}\text{C}^{18}\text{O}$ mixture, H_2^{18}O , and D_2^{18}O . The results are presented in **Figure 6** for the C-O stretching region and in **Figure S3** for the Ti-OH stretching region and they are reported in **Table 1**. With the CO isotopes, the 1931.7 and 1926.3 cm^{-1} absorptions shift to 1889.0 and 1883.7 cm^{-1} with $^{13}\text{C}^{16}\text{O}$, and to 1887.5 and 1882.3 cm^{-1} with $^{12}\text{C}^{18}\text{O}$ (**Figure 6**). With the $^{12}\text{C}^{16}\text{O}+^{12}\text{C}^{18}\text{O}$ mixture, the spectrum only provides the sum of each isotopic band, implying that one CO unit is involved in this mode. The bands at 2039.9 and 1911.4 cm^{-1} shift to 1994.0 and 1869.6 cm^{-1} with $^{13}\text{C}^{16}\text{O}$, and to 1993.5 and 1865.3 cm^{-1} with $^{12}\text{C}^{18}\text{O}$. With a $^{12}\text{C}^{16}\text{O}+^{12}\text{C}^{18}\text{O}$ mixture, further bands appear at 2020.7 and 1884.2 cm^{-1} , which is appropriate for the presence of two carbonyl groups in this molecule. With the D_2O isotope, the C-O stretching absorptions shift very slightly (**Table 1**) and the 1577.4, 1543.8, and 1549.4 cm^{-1} absorptions shift to 1138.4, 1120.4, and 1116.9 cm^{-1} . The band at 702.6 cm^{-1} in the Ti-OH region shifts to 657.2 and 656.3 cm^{-1} with the H_2^{18}O and D_2O isotopes, respectively (**Table 1** and **figure S3**).

Figure 6. Infrared spectra in the C-O stretching regions of the $\text{Ti}+\text{CO}+\text{H}_2\text{O}$ reaction products with $\text{Ti}/\text{CO}/\text{H}_2\text{O}/\text{Ar}=0.3/20/10/100$ for the isotopes (a) CO, (b) ^{13}CO , (c) C^{18}O , and (d) $\text{CO}+\text{C}^{18}\text{O}$.

Also, at this point, the experimental data alone have already given some general picture for the molecular shape for the two observed species. The two species have a Ti-H bond since we observed the bands at 1577.4 and 1549.4 cm^{-1} , and one of these species has a Ti-OH bond since we observed a band at

702.6 cm^{-1} . These absorptions are very close to the Ti-H and Ti-OH stretching vibrations observed at 1538.9 and 699.4 cm^{-1} , respectively, in the HTiOH molecules¹⁴. Since we also observe bands in the C-O stretching region, the two species could be considered like a HTiOH molecule with one and two CO molecules coordinated to the Ti atom as a HTiOH-CO and HTiOH-(CO)₂ structure.

THEORETICAL CALCULATIONS

Quantum chemical calculations have been performed to determine the molecular structures and to support the vibrational frequency analysis of the observed molecules. Previous theoretical works by Zhou and co-workers, using B3LYP functionals, on the Ti+H₂O reaction showed that HTiOH has a ³A'' ground state¹⁴ and that two reaction paths are possible on the singlet surface. One path is the hydrogen atoms transfer from oxygen to the metal center to form H₂TiO with ¹A'' ground state, and the other path leads to H₂ elimination to form the TiO monoxide.

Figure 7. Optimized geometrical parameters (distance in Å and angles in degrees) and ZPE corrected binding energy (in kcal/mol) for the ground state of the HTiOH and HTiOH-CO molecules.

HTiOH-CO: The B3LYP calculations predict that HTiOH-CO is a stable molecule in the ³A'' ground electronic state with a pseudo D_{3h} symmetry planar structure (**Figure 7**). Binding energy corrected for the zero point energy has been calculated to be -18.5 kcal/mol with respect to E(HTiOH) + E(CO). The H-Ti-O angle is 124.9°, smaller than that in HTiOH by 9°. The C-O and Ti-C bond lengths are 1.14 and 2.15 Å and the Ti-H, Ti-O, and O-H bond lengths are almost equal in HTiOH-CO and HTiOH. The calculated

vibrational frequencies corresponding to the observed bands are listed in **Table 2**. The C-O, Ti-H and Ti-OH stretching frequencies are calculated at 2063, 1574, and 761 cm^{-1} , and the H-Ti-O out of plane bending mode is calculated at 317 cm^{-1} .

HTiOH-(CO)₂: the DFT calculations show that HTiOH-(CO)₂ molecule has singlet electronic state ¹A with a pseudo T_d symmetry (**Figure 8**). Binding energy corrected for the zero point energy has been calculated to be -23.2 kcal/mol with respect E(HTiOH-CO) + E(CO). The two carbonyls groups are equivalent and the C-O bond length slightly increases by 0.002 Å compared to the HTiOH-CO. The Ti-C bond length shows a decrease of about 0.07 Å (Ti-C=2.08 Å). The O-H, C-O symmetric and antisymmetric, Ti-H and Ti-OH stretching frequencies are calculated at 3911, 2104, 2026, 1628, and 778 cm^{-1} (**Table 3**). For these two molecules a complete listing of all of the calculated frequencies is provided in the Supporting Information.

Figure 8. Optimized geometrical parameters (distance in Å and angles in degrees) and ZPE corrected binding energy (in kcal/mol) for the ground state of the HTiOH-(CO)₂ molecule.

Bonding analysis

The Laplacian isolines of the charge density enable us to identify regions where the charge density is concentrated (blue bullet in **Figure 9**). Consequently, we can easily find the most favorable direction for a

nucleophilic attack. Such a direction is shown by arrows in Figure 9. Preferred direction for the interaction between CO and HTiOH leads to a planar structure (Figure 9-b). Note that between two electrophilic (indicated by arrows in Figure 9-b) regions located on the HTiOH-CO complex only one could accommodate an electron-rich region of another molecule. That is the addition of a second CO modifies the position of the first CO within the possible angle imposed by the two charge-concentration regions ($\approx 200^\circ$) located on the Ti atom. As shown in Figure 9-c, the fact that the Ti atom is able to form a tetrahedral structure when its coordination sphere is completed with 4 ligands could be understood by the spatial organization of charge-concentration and charge-depletion regions. It is worth noting that all four valence electrons around Ti pair to give a tetra-coordinated species in the spin singlet state, when Ti center is tetra-ligated, while HTiOH-CO has a triplet state with two unpaired α electrons delocalized on the Ti and C atoms.

Figure 9. Isocurves of the Laplacian of the electronic density ($\nabla^2\rho < 0$, blue lines) for three compounds. Regions of charge concentration are indicated by blue bullet. The green bullet is the bond critical points. Electrophilic regions corresponding to the charge depletion are shown by arrows. Successive addition of CO molecule is also indicated.

Thanks to the presence of two σ -ligands (H and OH), the formal oxidation state of Ti is +2 within both HTiOH-CO and HTiOH-(CO)₂. Thus, monomeric Ti(II), with two d-electrons, forms either a paramagnetic complex with two unpaired electrons when one carbonyl is added to HTiOH, or a diamagnetic complex with $\alpha\beta$ paired electrons when two carbonyls are added to HTiOH. For HTiOH-(CO)₂, the Ti(II) center has a

total 10 electrons (four electrons donated by two CO π -ligands) which is clearly less than 18 electrons²⁷. Accordingly, the HTiOH-(CO)₂ complex presents actually a coordinative unsaturation with respect to 16/18 electron-rule so that it is able to accommodate additional CO. Nevertheless, we want to emphasize the fact that the singlet ground state is obtained for the experimentally observed HTiOH-(CO)₂ which is thermally quite stable: the calculated Gibbs free energy of formation per carbonyl was found to be $\Delta G(\text{HTiOH}-(\text{CO})_2) = -11.5 \text{ kcal/mol}$.

It is well established that the charge density at bond critical point is a good descriptor to estimate the bond strength^{28,29}. In going from HTiOH-CO to HTiOH-(CO)₂, the charge density at the C–O bond critical point slightly decreases from 0.486 to 0.484 e , while it increases for the C–Ti bond critical point (0.071 vs. 0.086 e). These trends are consistent with the change in the binding energy (-19.7 vs. -25.4 kcal/mol), the C–O bond length (1.140 vs. 1.142 Å), and the C–Ti bond distance (2.15 vs. 2.08 Å) resulted from the successive addition of CO to HTiOH.

Vibrational analysis and comparison with calculations.

All the experimentally observed vibrational frequencies for various isotopic substitutions as well as corresponding DFT - calculated harmonic wavenumbers, and the relative infrared intensities are listed in Table 2 and 3. The calculated frequency shifts due to the isotopic $^{12}\text{C}^{16}\text{O}/^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{16}\text{O}/^{12}\text{C}^{18}\text{O}$, $\text{H}_2\text{O}/\text{H}_2^{18}\text{O}$ and $\text{H}_2\text{O}/\text{D}_2^{18}\text{O}$ substitutions agree well with the experimental values for the two observed molecules. The observation of very weak shifts with isotopic labeled $^{13}\text{C}^{16}\text{O}+\text{H}_2^{16}\text{O}$ and $^{12}\text{C}^{16}\text{O}+\text{H}_2^{18}\text{O}$ and of large shifts with $^{12}\text{C}^{16}\text{O}+\text{D}_2^{18}\text{O}$ confirms the assignments for the Ti-H and Ti-OH stretching modes. On the basis of concentration and annealing effects, we can attribute the band in far infrared at 330.4 cm^{-1} to HTiOH-CO. We have two calculated bands at 317 and 318 cm^{-1} corresponding to γ_{HOTiH} and δ_{TiOH} bending modes but the calculated $\text{H}_2\text{O}/\text{D}_2^{18}\text{O}$ frequency shifts are 52 and 29 cm^{-1} , respectively. Since the experimental value is 54.9 cm^{-1} , we can attribute the band at 330.4 cm^{-1} to the γ_{HOTiH} bending mode. Accounting for the detectivity of the argon matrix setup, only modes with intensities larger than 35 km/mol are likely to be observed. For

HTiOH-CO, in addition to the bands in Table 2, six other vibrational frequencies have been calculated to have an IR intensity greater than 35 Km/mol at 255, 284, 318, 345, 418, and 3914 cm^{-1} , but the corresponding spectral regions are congested by strong absorptions of water and Ti+H₂O reaction products.

Table 2. Comparison between experimental frequencies and calculated harmonic data (in cm^{-1}) of the observed HTiOH-CO molecule with the isotopic Shifts.

Experimental					DFT					Modes
¹² C ¹⁶ O	¹³ C ¹⁶ O	¹² C ¹⁸ O	H ₂ ¹⁸ O	D ₂ ¹⁸ O	¹² C ¹⁶ O	¹³ C ¹⁶ O	¹² C ¹⁸ O	H ₂ ¹⁸ O	D ₂ ¹⁸ O	
1926.3(100) ^a	42.6	44.0	0.2	2.8	2063(100) ^a	47	49	0	1	ν_{CO}
1543.8(34)	0.4	0.5	0.2	426.9	1574(51)	0	0	0	448	$\nu_{\text{Ti-H}}$
702.6(15)	-	0.6	27.7	45.7	761(23)	0	0	27	46	$\nu_{\text{Ti-OH}}$
330.4(17)	2.9	0.8	1.4	54.9	317(16)	4	2	2	52	γ_{HOTiH}

^arelative infrared intensities in parenthesis normalized with respect to the CO mode.

Absorption bands observed at 1931.7 and 1926.3 cm^{-1} are assigned to two sites of CO stretching mode of HTiOH-CO, and the two absorptions at 2039.9 and 1911.4 cm^{-1} have been assigned to symmetric and antisymmetric CO stretching modes of HTiOH-(CO)₂. Furthermore the calculated frequency shifts due to the ¹²C¹⁶O/¹³C¹⁶O and ¹²C¹⁶O/¹²C¹⁸O isotopic substitutions agree well with experimental values and give strong support for the assignment of these bands. Finally, the O-H stretching mode of HTiOH-CO is not observed but that of HTiOH-(CO)₂ is observed at 3745.5 cm^{-1} .

Table 3. Comparison between experimental frequencies and calculated harmonic data (in cm^{-1}) of the observed HTiOH-(CO)₂ molecule with the isotopic Shifts.

Experimental					DFT					Modes
¹² C ¹⁶ O	¹³ C ¹⁶ O	¹² C ¹⁸ O	H ₂ ¹⁸ O	D ₂ ¹⁸ O	¹² C ¹⁶ O	¹³ C ¹⁶ O	¹² C ¹⁸ O	H ₂ ¹⁸ O	D ₂ ¹⁸ O	
3745.5(12) ^a	0.1	0	12.0	-	3911(19) ^a	0	0	13	1079	ν_{OH}

2039.9(13)	45.9	46.4	0.1	1.0	2104(30)	48	49	0	1	ν_{CO} sym
1911.4(100)	41.8	46.1	0	0.6	2026(100)	45	48	0	0	ν_{CO} asym
1577.4(17)	0.1	0.1	0	439.0	1628(38)	0	0	0	463	ν_{TiH}

^arelative infrared intensities in parenthesis normalized with respect to the CO mode.

Under the present experimental conditions, Ti atoms react with H₂O and CO mixtures in solid argon. Since our thermal evaporation experiments indicate that the ground state titanium atoms do not react with CO spontaneously to form TiCO molecule, the first step of the reaction must start by the reaction between Ti and water, and we know that this reaction produces HTiOH spontaneously. The HTiOH molecule is produced mainly from reaction (1) during deposition:

The HTiOH-CO molecule was formed by reaction (2). Our experimental observations suggest that the HTiOH-CO is formed by reaction of HTiOH and CO whereas HTiOH-(CO)₂ species is formed via CO addition (reaction (3)).

Owing to the cooperativity effect, addition of a second carbonyl is more stabilizing by 5.7 kcal/mol than that of the first CO ligand.

CONCLUSION

The reactions of thermal evaporated titanium atoms with water and carbon monoxide have been investigated using argon matrix isolation infrared absorption spectroscopy and density functional calculations. Results show that the inserted HTiOH molecule spontaneously reacts with CO to form the HTiOH-CO molecule with planar structure in the ground triplet electronic state. The mono-ligated adduct reacts in turn with a second CO molecule to form HTiOH-(CO)₂. The experimental data, with the help of

isotopic effects, are fully supported by theoretical calculations. Bonding analysis within the QTAIM topology allowed us to rationalize the pseudo tetrahedral structure of the di-ligated HTiOH-(CO)₂ compound. Particularly, we showed that the perfect spin pairing takes place when the coordination sphere of Ti(II) center is complemented by four ligands.

Supporting information

Infrared spectra in the Ti-H and O-H stretching regions with two different CO/Ar molar ratios (Figure S1); Infrared spectra in the (a) after deposition at 12 K and (b) after annealing to 32 K (Figure S2); Isotopic study in the Ti-OH region for the isotopes (a) CO/H₂O, (b) CO/H₂¹⁸O, and (c) CO/H₂¹⁸O after annealing to 25 K (Figure S3); Calculated harmonic frequencies (cm⁻¹) and intensities (km/mol) for the HTiOH, HTiOH-CO, and HTiOH-(CO)₂ molecules (Table S1).

TOC Graphic

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