SUPPORTING INFORMATION (JP 0360974)

Structure and Vibrational Spectrum of Formate and Acetate Adsorbed from Aqueous Solution onto the TiO_2 Rutile (110) Surface

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Figure Captions

Fig. S1

Perspective view of (a) the η^2–$(HCOO)TiF_4^-$ and (b) the η^2–$(HCOO)TiF_4 \cdot (H_2O)_2^-$ complexes.

Fig. S2

Perspective view of (a) the η^1–$(HCOO)TiF_5^{2-}$ complex and (b), (c) two isomers of the η^1–$(HCOO)TiF_5 \cdot H_2O^{2-}$ complexes.

Fig. S3

Perspective view of the η^2–$(HCOO)TiF_4 \cdot H_2O^-$ complex.

Fig. S4

Perspective view of the μ–$(HCOO)Ti_2O_2F_6^{3-}$ cluster.

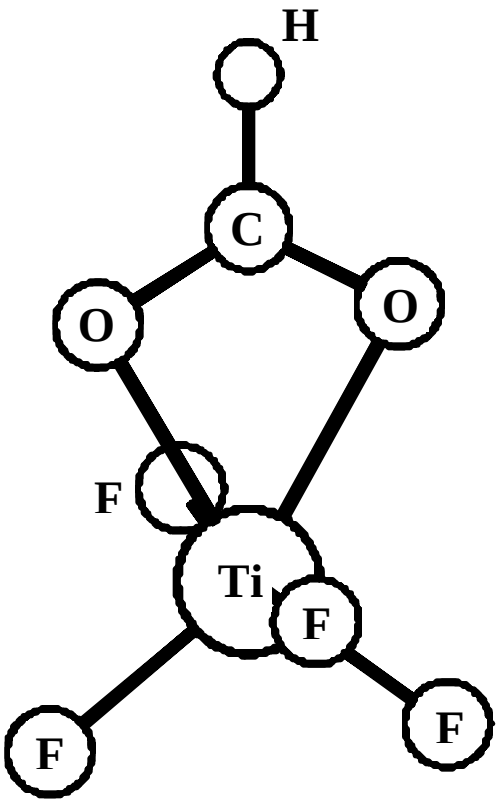

Fig. S1a

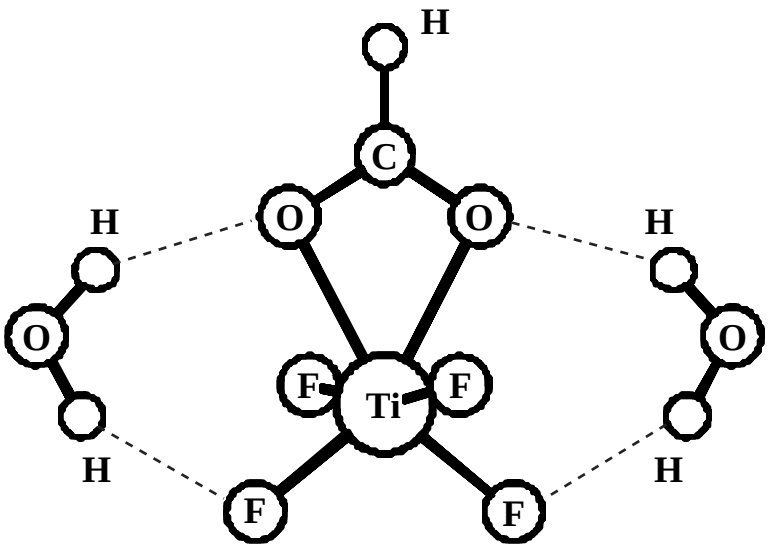

Fig. S1b

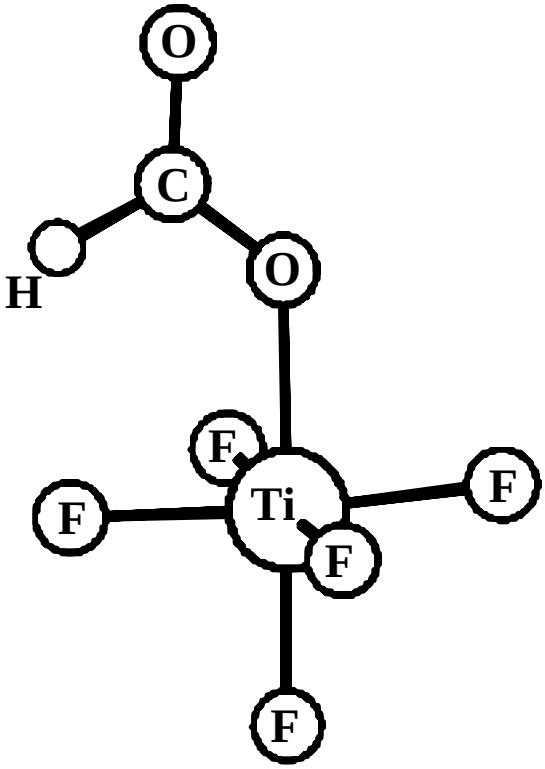

Fig. S2a

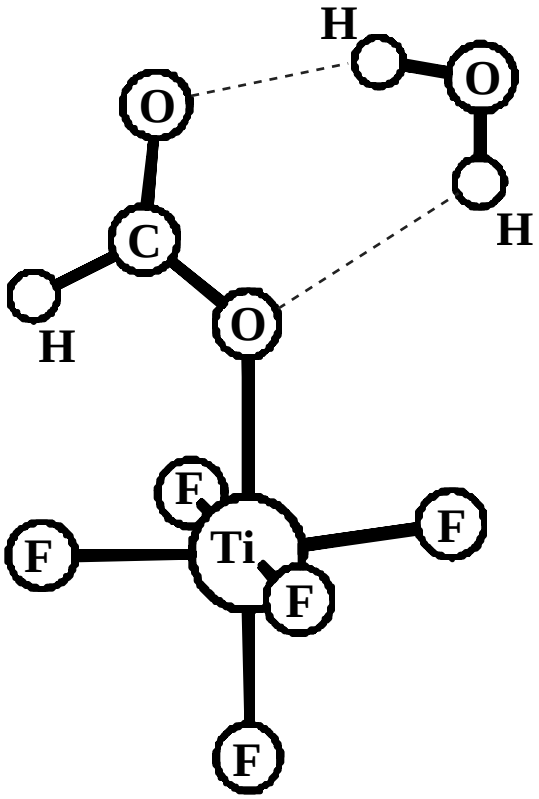

Fig. S2b

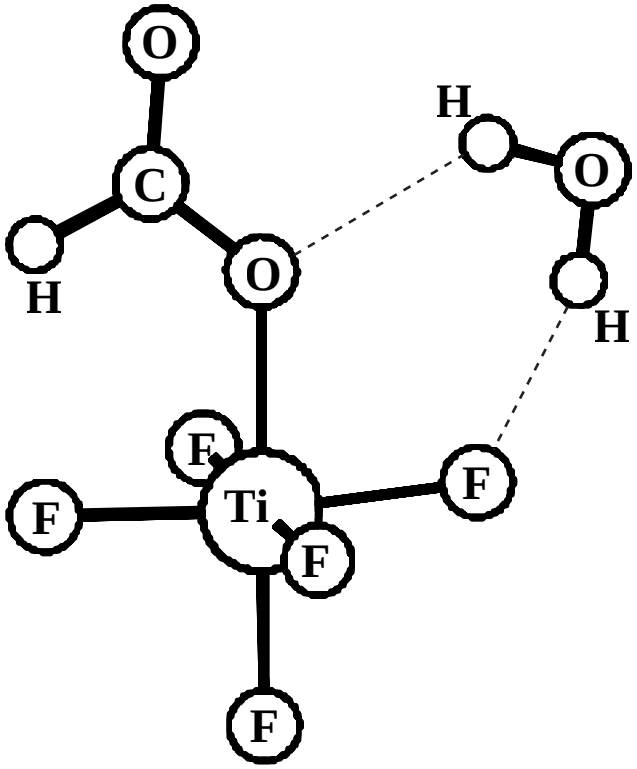

Fig. S2c

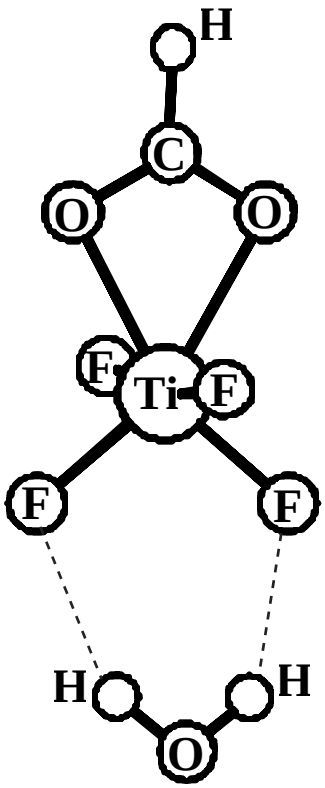

Fig. S3

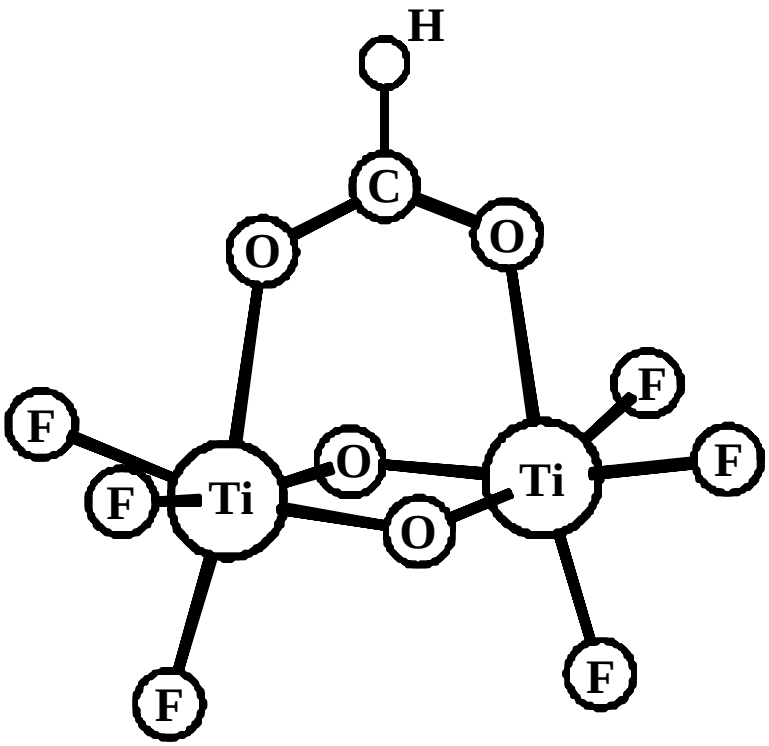

Fig. S4

TABLE S1: Observed[51-53] and Calculated Vibrational Frequencies (cm^{-1}) of *cis* and *trans*-HCOOH.

	trans		*cis*	
mode	obsd	calcd	obsd[a]	calcd
ν(OH)	3551	3606	3618	3665
ν(CH)	2953	2953	2899	2864
ν(C=O)[b]	1767	1814	1808	1856
δ(HCO)	1381	1387	1396(?)	1417
δ(HOC)	1216	1282	1244	1273
ν(C-O)[c]	1103	1141	1108	1096
π(H-COO)	1037	1064		1053
π(H-OCO)	635	647	503	466
δ(OCO)	629	622	661	653

[a]In a solid Ar matrix. [b]Or ν_{as}(COO). [c]Or ν_{s}(COO).

TABLE S2: Calculated Vibrational Frequencies of η^2-(HCOO)Ti Model Compounds.

	modes,[a] cm^{-1}							
	δ(OCO)	π(H-COO)	ν_s(COO)	δ(HCO)	ν_{as}(COO)	ν(CH)	d(Ti–OOCH), Å	$\Delta\nu_{as\text{-}s}$, cm^{-1}
η^2-(HCOO)TiF_4^-	822 (814)	1082 (924)	1398 (1362)	1312 (977)	1612 (1591)	2898 (2148)	2.191	214 (229)
η^2-(HCOO)$TiF_4 \cdot (H_2O)_2^-$ [b]	825 (817)	1081 (922)	1399 (1363)	1308 (975)	1599 (1577)	2932 (2175)	2.186	200 (214)
η^2-(HCOO)TiF_5^{2-} [c]	782 (773)	1076 (926)	1388 (1365)	1354 (1001)	1695 (1682)	2588 (1903)	2.662	307 (317)
trans-η^2-(HCOO)$TiF_4(OH_2)^-$ [c]	826 (818)	1083 (925)	1412 (1376)	1308 (974)	1633 (1613)	2870 (2127)	2.223	221 (237)

[a]In parenthesis: frequencies for the corresponding $DCOO^-$ compound. [b] Each of the two H_2Os forms one H-bond to the formate, and one H-bond to the F^- anion. [c]Saddlepoint with one imaginary frequency.

TABLE S3: Calculated Vibrational Frequencies of η^1-(HCOO)Ti Model Compounds.

	modes,[a] cm^{-1}							
	δ(OCO)	π(H-COO)	ν_s(COO)	δ(HCO)	ν_{as}(COO)	ν(CH)	d(Ti–OOCH), Å	$\Delta\nu_{as\text{-}s}$, cm^{-1}
η^1-(HCOO)TiF_5^{2-}	777 (770)	1098 (941)	1324 (1308)	1401 (1027)	1687 (1671)	2807 (2071)	2.083	363 (363)
η^1-(HCOO)Ti $F_5 \cdot H_2O^{2-}$ [b]	786 (779)	1099 (940)	1340 (1321)	1387 (1019)	1663 (1647)	2844 (2100)	2.098	323 (326)
η^1-(HCOO)Ti $F_5 \cdot H_2O^{2-}$ [c]	781 (773)	1097 (939)	1318 (1304)	1398 (1024)	1676 (1662)	2828 (2088)	2.087	358 (358)
trans-η^1-(HCOO)$TiF_4(OH)^{2-}$	773	1098	1330	1400	1684	2793	2.102	354
trans-η^1-(HCOO)$TiF_4(OH)^{2-}$ [d]	774	1096	1329	1400	1685	2782	2.108	356
trans-η^1-(HCOO)$TiF_4(OH_2)^-$	795 (786)	1080 (921)	1228 (1224)	1408 (1024)	1758 (1732)	2869 (2128)	1.898	530 (508)
trans-η^1-(HCOO)$TiF_4(OH_2)^-$ [d]	794	1080	1228	1407	1758	2865	1.899	530
cis-η^1-(HCOO)$TiF_4(OH)^{2-}$ [e]	737 (730)	1080 (929)	1360 (1341)	1401 (1033)	1685 (1674)	2639 (1941)	2.161	325 (333)
cis-η^1-(HCOO)$TiF_4(OH)^{2-}$ [f]	776 (769)	1101 (943)	1328 (1310)	1397 (1025)	1684 (1668)	2815 (2077)	2.125	356 (358)
cis-η^1-(HCOO)$TiF_4(OH_2)^-$ [e]	738 (732)	1083 (926)	1350 (1333)	1393 (1024)	1657 (1645)	2829 (2091)	2.056	307 (312)
cis-η^1-(HCOO)$TiF_4(OH_2)^-$ [f]	746 (738)	1070 (916)	1282 (1274)	1409 (1031)	1749 (1729)	2763 (2043)	2.037	467 (455)
cis-η^1-(HCOO)$TiF_3(OH_2)_2$ [e,g]	723 (718)	1079 (919)	1293 (1285)	1386 (1015)	1688 (1669)	2923 (2168)	1.954	395 (384)
η^1-(HCOO)TiF_4^-	744	1073	1282	1401	1734	2795	1.992	452
η^1-(HCOOH)TiF_5^-	672 (666)	1048 (890)	1118 (1162)	1424 (993)	1804 (1769)	2997 (2238)	2.398	686 (607)

[a]In parenthesis: frequencies for the corresponding $DCOO^-$ compound. [b] H_2O forms two H-bonds to each oxygen of $HCOO^-$. [c] H_2O forms one H-bond to $HCOO^-$, and one H-bond to F^-. [d]Another conformer. [e]H-bonded to C=O. [f]H-bonded to C-O. [g]The H_2O ligands are trans to each-other.