Support Information

Reactions of Vanadium Dioxide Molecules with Acetylene: Infrared Spectra of $VO_2(\eta^2\text{-}C_2H_2)_x$ (x=1, 2) and OV(OH)CCH in Solid Neon

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TABLE S1: Infrared Absorptions (in cm^{-1}) from Codeposition of Laser-Evaporated Vanadium oxides with Acetylene in Excess Neon.

C_2H_2	$^{13}C_2H_2$	C_2D_2	$H^{12}C^{13}CH$	assignment
998.8	998.8	998.8	998.8	VO (VO str.)
947.5	947.5	947.5	947.5	VO_2 (OVO asym. str.)
958.1	958.1	958.1	958.1	VO_2 (OVO sym. str.)
3296.7	3280.7	2439.5	3285.5	C_2H_2 (C-H asym. str.)
731.9	730.0	540.0	731.0	C_2H_2 (C-H bend.)
3249.5				$VO_2(\eta^2-C_2H_2)$ (sym. str.)
3184.7	3175.5	2364.0	3178.8	$VO_2(\eta^2-C_2H_2)$ (C-H asym. str.)
1797.3	1738.1	1638.6	1768.2	$VO_2(\eta^2-C_2H_2)$ (C≡C str.)
954.3	954.3	954.3	954.3	$VO_2(\eta^2-C_2H_2)$ (OVO sym. str.)
960.0	960.1	959.6	960.1	$VO_2(\eta^2-C_2H_2)$ (OVO asym. str.)
684.5	681.0	502.1	684.3	$VO_2(\eta^2-C_2H_2)$ (Out-of-plane sym. C-H wag.)
655.4	655.7	481.1	655.9	$VO_2(\eta^2-C_2H_2)$ (in-plane sym. C-H wag.)
623.2	619.3	481.1	621.0	$VO_2(\eta^2-C_2H_2)$ (in-plane sym. C-H wag.)
3227.1	3218.3	2395.0	3222.5	$VO_2(\eta^2-C_2H_2)_2$ (C-H asym. str.)
3224.3	3215.2	2393.1		$VO_2(\eta^2-C_2H_2)_2$ (C-H asym. str.)
1872.0	1811.0	1693.8	1841.9	$VO_2(\eta^2-C_2H_2)_2$ (C≡C sym. str.)
1854.2	1793.8	1679.1	1824.4	$VO_2(\eta^2-C_2H_2)_2$ (C≡C asym. str.)
955.9	955.9	955.9	955.9	$VO_2(\eta^2-C_2H_2)_2$ (OVO sym. str.)
949.4	949.4	949.0	949.4	$VO_2(\eta^2-C_2H_2)_2$ (OVO asym. str.)
706.6	704.1		704.3	$VO_2(\eta^2-C_2H_2)_2$ (0ut-of-plane sym. C-H wag.)
3718.2	3718.0	2741.1	3718.1	OV(OH)CCH (O-H str.)
1969.7	1899.4	1855.9	1942.0, 1928.1	OV(OH)CCH (C≡C str.)
1030.8	1030.3	1030.2	1030.6	OV(OH)CCH (V=O str.)
764.9	764.5	749.7	764.6	OV(OH)CCH (V-OH str.)
691.4	685.8		687.0, 691.2	OV(OH)CCH (in-plane C-H wag.)
663.4	658.0		658.3, 662.7	OV(OH)CCH (out-of-plane C-H wag.)
500.0	490.0	486.8	496.0, 493.6	OV(OH)CCH (V-C str.)
2082.7	2023.6	2069.4	2070.1, 2029.8	V(H)CCO (CCO str.)
2031.5	1986.0	2029.9	2031.5, 1986.0	XVCO (C=O str.)

TABLE S2: Calculated Total Energies (in Hartrees, after Zero Point Energy Correction), Vibrational Frequencies (cm^{-1}) and Intensities (km/mol) of Various Species Involved in the VO_2+ C_2H_2 Reactions

Molecule	Energy	Frequency(intensity)
C_2H_2 ($^1\Sigma_g^+$)	-77.329684	3527.4(0), 3424.8(94), 2062.5(0), 769.5(112), 769.5(112), 644.2(0), 644.2(0)
VO_2 ($^2A_1$)	-1094.504441	1027.0(34), 996.7(427), 261.6(4)
$VO_2(\eta^2\text{-}C_2H_2)$ ($^2B_2$)	-1171.874537	3388.7(50), 3307.6(107), 1880.5(96), 1037.7(122), 1036.4(391), 707.7(69), 697.0(23), 668.5(0), 645.6(67), 357.5(1), 347.8(10), 295.7(6), 151.8(0), 124.1(0), 57.2(69)
$VO_2(\eta^2\text{-}C_2H_2)_2$ (^2A)	-1249.231189	3454.4(7), 3452.3(80), 3365.1(130), 3363.8(76), 1956.8(37), 1939.6(84), 1020.3(95), 1002.3(328), 759.4(4), 743.1(105), 741.7(2), 681.1(4), 664.1(8), 654.6(11), 643.4(1), 633.8(5), 364.3(1), 336.3(10), 315.8(3), 269.8(9), 220.0(8), 167.9(1), 158.9(13), 147.5(0), 134.8(2), 47.0(2), 47.0(1)
OV(OH)CCH ($^2A''$)	-1171.894872	3898.6(218), 3447.3(35), 2040.1(68), 1090.5(284), 729.9(256), 718.8(20), 695.2(49), 488.0(67), 336.4(135), 314.7(156), 254.1(51), 237.3(19), 220.8(3), 112.6(11), 101.0(3)
TS	-1171.844088	3368.4(71), 1925.1(24), 1640.1(78), 1083.4(145), 1062.1(166), 893.4(141), 732.8(61), 672.1(71), 594.0(8), 362.3(40), 241.4(8), 197.9(6), 167.7(2), 72.8(44), 1400.0i(1673.3)
V(H)CCO ($^5A''$)	-1095.968952	3194.5(18), 2144.5(1215), 1239.3(11), 934.8(147), 619.5(32), 580.9(4), 456.3(21), 381.3(64), 90(1)

Cartesian Coordinates of the Structures of Various Species Involved in the VO_2+ C_2H_2 Reactions

C_2H_2 ($D_{\infty h}$, $^1\Sigma_g^+$)

C	0.00000000	0.00000000	0.59967200
H	0.00000000	0.00000000	1.66225700
C	0.00000000	0.00000000	-0.59967200
H	0.00000000	0.00000000	-1.66225700

VO_2 (C_{2v}, $^2A_1$)

V	0.00000000	0.00000000	0.35133400
O	0.00000000	1.36399800	-0.50504200
O	0.00000000	-1.36399800	-0.50504200

$VO_2(\eta^2\text{-}C_2H_2)$ (C_{2v}, $^2B_2$)

V	0.00000000	0.00000000	0.33405900
O	1.37073900	0.00000000	1.16750900
O	-1.37073900	0.00000000	1.16750900
C	0.00000000	0.61444000	-1.83929600
C	0.00000000	-0.61444000	-1.83929600
H	0.00000000	1.64168100	-2.14597800
H	0.00000000	-1.64168100	-2.14597800

$VO_2(\eta^2\text{-}C_2H_2)_2$ (C_2, ^2A)

V	0.00134100	-0.34117200	0.00086800
O	-0.05438100	-1.21526400	-1.35322400
O	0.05308000	-1.21057300	1.35787900
C	-1.54861600	1.47623300	0.14863300
C	-2.16039500	0.44329000	-0.05011600
H	-2.81995200	-0.37658000	-0.23479300
H	-1.24457500	2.47696900	0.35787800
C	1.54564200	1.47744100	-0.14865100
C	2.15999600	0.44435700	0.04229300
H	2.82403800	-0.37390200	0.21789000
H	1.24030300	2.47923500	-0.35112300

OV(OH)CCH (C_s, $^2A''$)

V	0.00000000	0.41959400	0.00000000
O	-1.28654800	1.32550500	0.00000000
O	1.67991500	1.09415100	0.00000000
H	2.55659900	0.70109800	0.00000000
C	-0.34952600	-1.55232700	0.00000000
C	-0.49608000	-2.76262300	0.00000000
H	-0.62989300	-3.81929900	0.00000000

TS (C_1, ^{2}A)

H	-1.09752500	1.31815400	0.16808800
C	-1.88820000	0.22225300	0.14873400
C	-1.68150300	-0.99635100	0.02916400
H	-1.80915000	-2.05969800	-0.00558000
V	0.40840900	-0.04958000	-0.18163900
O	1.73449700	-0.79632200	0.27073400
O	0.13193800	1.61213100	0.09774000

V(H)CCO (C_s, ^{5}A″)

C	0.00000000	0.98741600	0.00000000
C	1.28285600	0.75263800	0.00000000
O	2.41081400	0.44514000	0.00000000
V	-1.15593500	-0.69550600	0.00000000
H	-0.39713400	1.99518500	0.00000000