Supplementary information .

Tables of the bands and their assignments for different increments of NH_3 introduced onto the solids.

	Starting Material	1st Aliquot	2nd Aliquot	3rd Aliquot	4th Aliquot	5th Aliquot	6th Aliquot	7th Aliquot	Assignments	References
GP350-S-1N	1122(w), 1171(vw)	1122(w), 1171(vw)	1122(w), 1171(vw)	1122(w), 1171(vw)	1122(w), 1171(vw)	1122(w), 1171(vw)	1122(sh,w), 1171(vw)		ν(S-O) in tri-dentate and bi-dentate sulfates	[7, 8]
							1126(w)	1126(w)	$\delta^{sym}(NH_3)$	[3,6]
	1382 (vs)	1382 (vs)	1382 (vs)	1382 (vs)	1382 (vs)	1382 (vs)	1360(sh,m), 1382 (m)	1360(sh,m), 1382 (m)	ν(S=O) in di-sulfates	[1,2]
	1610 cm^{-1} (t)	1610 cm^{-1} (t)	1610 cm^{-1} (t)	1610 cm^{-1} (t)	1610 cm^{-1} (t)	1610 cm^{-1} (t)	1610 cm^{-1} (vw)	1609cm^{-1}(vw)	$\delta(H_2O)$	[11]
	2720(t),2820(t), 2850(t), 2920(t), 2950(t)	2720(t),2820(t), 2850(t), 2920(t), 2950(t)	2720(t),2820(t), 2850(t), 2920(t), 2950(t)	2720(t),2820(t), 2850(t), 2920(t), 2950(t)	2720(t),2820(t), 2850(t), 2920(t), 2950(t)	2720(t),2820(t), 2850(t), 2920(t), 2950(t)	2720(t),2820(t), 2850(t), 2920(t), 2950(t)	2720(t),2820(t), 2850(t), 2920(t), 2950(t)	ν(C-H)	[9]
	3200 (t)	3200 (t)	3200 (w)	3200 (w)	3200 (w)	3200 (w)	3200 (w)	3200 (w)	ν(OH) of H_2O	[11]
		3263(vw), 3352(vw), 3388(vw)	3263(vw), 3352(vw), 3388(vw)	3263(vw), 3352(vw), 3388(vw)	3263(vw), 3352(vw), 3388(vw)	3263(w), 3352(w), 3388(w)	3263(w), 3352(w), 3388(w)	3263(w), 3352(w), 3388(w)	ν(NH) of NH_3	[11]
	3640 (t)								ν(OH) associated to di-sulfate species	[1]
		3652 (t)	3652 (w)	3652 (w)	3652 (w)	3652 (w)	3652 (w)	3652 (w)	ν(OH) associated to di-sulfate species	[1]
	3665(t)								ν(OH) on anatase for –OH groups bonded to each other by hydrogen bridges and situated in adjacent unit cells	[10]
	3688(vw)								ν(OH) on rutile for –OH isolated (Ti^{4+})	[10]
	3717(vw), 3736(vw),	3717(vw), 3736(vw)	3717(vw), 3736(vw)	3717(vw), 3736(vw)	3717(vw), 3736(vw)	3717(vw), 3736(vw)	3717(vw), 3736(vw)	3717(vw), 3736(vw)	ν(OH) on anatase for –OH isolated (Ti^{4+})	[10]

GP350-S-1N	8th Aliquot	9th Aliquot	10th Aliquot	11th Aliquot	12th Aliquot	Saturation with 1 torr of NH_3	After treatment under vacuum	Assignments	References
	1126(m)							$\delta^{sym}(NH_3)$	[3,6]
		1130 (m)	1130 (m)	1130 (m)	1130 (m)	1130 (m)	1130 (m)	ν(S-O) in Monosulfates	[4, 5]
		1250(w), 1315(w), 1605(w)	1250(w), 1315(w), 1605(w)	1250(w), 1315(w), 1605(w)	1250(w), 1315(t,sh), 1605(w)			adsorbed NH_3 on acidic sites	
	1360(sh,w), 1382 (w)							ν(S=O) in disulfates	[1,2]
		1440 (m)	1440 (m)	1440 (m)	1440 (m)	1440 (m)	1440 (m)	δ(NH)from ammonium salt, NH_4^+	[11]
	1608 cm^{-1} (t)	1606 cm^{-1} overlapped with adsorbed NH_3	1605 cm^{-1} (t)	1605 cm^{-1} (t)	1605 cm^{-1} (t)	1605 cm^{-1} (t)	1605 cm^{-1} (w)	$\delta^{asym}(NH_3^+)$	[11]
			2800(t), 2900(t), 3050(t)	2800(t), 2900(t), 3050(vw,b)	2800(t), 2900(t), 3050(vw,b)	2800(t), 2900(t), 3050(vw,b)	2800(t), 2900(t), 3050(vw,b)	ν(N-H) from NH_2+	[11]
	3300 (w)	3300 (m)	3300 (m)	3300 (w)	3300 (w)	3300 (w)	3300 (w)	ν(NH)from ammonium salt, NH_4^+	[11]
	3155(vw),3193(vw), 3262(vw),3350(vw), 3385(vw),	3155(w),3193(w), 3262(w),3350(w), 3385(w)	3155(w),3193(w), 3262(w),3350(w), 3385(w)	3155(w),3193(w), 3262(w),3350(w), 3385(w)	3155(w),3193(w), 3262(w),3350(w), 3385(w)	3155(w),3193(w), 3262(w),3350(w), 3385(w)	3155(w),3193(w), 3262(w),3350(w), 3385(w)	ν(NH) of NH_3^+	[11]
	3574(t)	3574(t)	3574(t)	3574(t)	3574(t)			ν(OH) associated to mono-sulfate species	
	3652(w)	3652 (vw)	3652(t)	3652(t)	3652(t)	3652(t)	3652(t)	ν(OH) associated to di-sulfate species	[1]
		3684(t)	3685(t)	3687(t)	3686(t)	3688(t)	3686(t)	ν(OH) on rutile for –OH isolated (Ti^{4+})	[10]

	Starting Material	1st Aliquot	2nd Aliquot	3rd Aliquot	4th Aliquot	5th Aliquot	6th Aliquot	7th Aliquot	Assignments	References
GP350					1046(vw)	1052(vw)	1057(vw)		ν(S-O)in monosulfate species	[5,7]
		1165(vw)	1165(vw)	1165(vw)	1164(vw)	1160(vw)	1156(vw)	1153(vw)	$\delta^{sym}(NH_3)$	[3,6]
	1260(t),1326(vw), 1362(vw)	1260(t),1326(vw), 1362(vw)	1260(t),1326(vw), 1362(vw)	1260(t),1326(vw), 1362(vw)	1260(t),1326(vw), 1362(vw)				Chelate BidendateNitrates	[12]
	1492(vw), 1557(vw), 1596(vw)	1492(vw), 1557(vw), 1596(vw)	1492(vw), 1557(vw), 1596(vw)	1492(vw), 1557(vw), 1596(vw)	1492(vw), 1557(vw), 1596(vw)	1492(vw), 1557(vw), 1596(vw)	1492(vw), 1557(vw), 1596(vw)	1492(vw), 1557(vw), 1596(vw)	Monodendate Nitrates	[12]
	1364 (w)	1364 (w)	1364(w)	1364 (w)	1364 (vw)	1364 (t)			ν(S=O) for di-sulfates	[1,2]
					1330(t,sh.)	1331(vw)	1324(vw)		ν(S–O) in monosulfate	[5,7]
	1601 cm^{-1} (t)	1607 cm^{-1} (t)	1608 cm^{-1} (t)	1610 cm^{-1} (w)	1603 cm^{-1} (t)	1600 cm^{-1} (t)	1598 cm^{-1} (vw)	1598cm^{-1} (vw)	$\delta(H_2O)$ overlapped with nitrates band at ca. 1596 cm^{-1}, and adsorbed $NH_3$with $\delta^{asym}(NH_3^+)$	[11]
	2673(t),2708(t), 2854(t), 2924(t), 2962(t)	2854(t), 2924(t), 2962(t)	2854(t), 2924(t), 2962(t)	2854(t), 2924(t), 2962(t)	2854(t), 2924(t), 2962(t)	2854(t), 2924(t), 2962(t)	2854(t), 2924(t), 2962(t)	2854(t), 2924(t), 2962(t)	ν(C-H)	[9]
	3200 (t)	3200 (t)	3200 (t)	3200 (w)	3200 (w)	3200 (w)	3200 (w)	3200 (w)	ν(OH) of H_2O	[11]
		3263(t),	3263(t), 3352(t), 3388(t)	3263(vw), 3352(vw), 3388(vw)	3263(vw), 3352(vw), 3388(vw)	3263(w), 3352(w), 3388(w)	3263(w), 3352(w), 3388(w)	3263(w), 3352(w), 3388(w)	ν(NH) of NH_3	[11]
				3570(t)	3570(t)	3570(t)	3570(t)	3570(t)	ν(OH) associated to mono-sulfate species	
	3640(t), 3671(t), 3688(t), 3717(t), 3736(t)	3640(t), 3671(t), 3688(t), 3717(t), 3736(t)	3640(t), 3671(t), 3688(t), 3717(t), 3736(t)	3640(t), 3671(t), 3688(t), 3717(t), 3736(t)	3640(t), 3671(t), 3688(t), 3717(t), 3736(t)	3671(w), 3717(t),			ν(OH) on anatase	[10]
							3687(t), 3663(w)	3687(t),3663(w)	ν(OH) on rutile for –OH isolated (Ti^{4+})	[10]

GP350	10th Aliquot	Saturation with 1 torr of NH_3	After treatment under vacuum	Assignments	References
	1161(w)	1161(w)	1161(w)	$\delta^{sym}(NH_3)$	[3,6]
			1297 (vw)	ν(S-O) in Monosulfates	[4, 5]
	1599(w)	1599(w)	1599(w)	$\delta^{asym}(NH_3^+)$,adsorbed NH_3 on acidic sites	[11]
	1485(vw), 1377(vw)	1484(vw), 1377(vw)	1493(vw), 1375(vw)	Monodendate Nitrates	[11]
	1608 cm^{-1} (t) overlapped with adsorbed NH_3	1606 cm^{-1} overlapped with adsorbed NH_3	1605 cm^{-1} (t) overlapped with adsorbed NH_3	δ(H20)	[11]
			2800(t), 2900(t), 3050(t)	ν(N-H) from NH_2+	[11]
	3200 (m)	3200 (m)	3200 (m)	ν(OH)	[11]
	3155(vw),3193(vw), 3262(vw),3350(vw), 3385(vw),	3155(w),3193(w), 3262(w),3350(w), 3385(w)	3155(w),3193(w), 3262(w),3350(w), 3385(w)	ν(NH) of NH_3^+	[11]
	3574(t)		3570(t)	ν(OH) associated to mono-sulfate species	
	3687(t), 3663(t)	3687(t), 3663(t)	3686(t), 3663(t)	ν(OH) on rutile for –OH isolated (Ti^{4+})	[10]

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