Supporting Information

Aqueous divalent metal – nitrate interactions: Hydration versus ion pairing

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Table 1 Curve-fitting results of the nitrate in-plane deformation modes from the Raman spectra.

	0.5 m		1 m				1.7 m				3.3 m				Saturated			
	Position	Area	Position		Area		Position		Area		Position		Area		Position		Area	
			#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2
NH_4NO_3*	718.0	6662	718.1		12623		718.2		21496		718.3		39324		718.2		88443	
$Mg(NO_3)_2$	719.0	8007	718.8		16535		719.9		21943		720.4		37953		720.1		48296	
$Ca(NO_3)_2$	719.0	10188	718.6	738.2	16241	3276	718.6	738.4	19972	5139	719.1	739.5	32589	10262	718.5	739.7	41380	23187
$Sr(NO_3)_2$	720.4	9429	717.8	732.3	14850	3926	717.9	733.5	19132	8478	718.4	734.9	33914	19443	718.4	734.9	33914	19443
$Pb(NO_3)_2$	721.1	6168	716.6	727.8	10327	6634	716.7	729.3	12673	10169	-	-	-	-	716.7	729.3	12673	10169

* NH_4NO_3 has the same nitrate concentration as other nitrate solutions. The concentrations for NH_4NO_3 solutions are 1 m, 2 m, 3.4 m, 6.6 m, and saturated or near saturation.

Table 2 Curve-fitting results of the nitrate symmetric stretching modes from the Raman spectra.

	0.5m		1.0m		1.7m		3.3m		Saturated	
	Position (cm^{-1})	FWHM (cm^{-1})	Position (cm^{-1})	FWHM (cm^{-1})	Position (cm^{-1})	FWHM (cm^{-1})	Position (cm^{-1})	FWHM (cm^{-1})	Position (cm^{-1})	FWHM (cm^{-1})
NH_4NO_3*	1047.9	7.9	1047.8	7.9	1047.8	8.0	1047.8	8.1	1047.6	8.5
$Mg(NO_3)_2$	1048.9	9.9	1048.9	10.3	1049.9	10.5	1050.5	11.1	1050.2	11.8
$Ca(NO_3)_2$	1048.7	10.2	1049.1	10.6	1049.9	11.0	1050.4	11.8	1050.3	12.8
$Sr(NO_3)_2$	1049.0	10.1	1049.5	10.7	1050.5	11.1	1050.6	12.1	1050.6	12.1
$Pb(NO_3)_2$	1046.9	12.2	1046.3	12.8	1046.1	13.0	-	-	1046.1	13.0

* NH_4NO_3 has the same nitrate concentration as other nitrate solutions. The concentrations for NH_4NO_3 solutions are 1 m, 2 m, 3.4 m, 6.6 m, and saturated.

Table 3 Curve-fitting results of the nitrate symmetric stretching modes from the infrared spectra shown in Figure 1 of this document.

	0.5m	1.0m	Saturated
	Position (cm^{-1})	Position (cm^{-1})	Position (cm^{-1})
$Mg(NO_3)_2$	1043.6	1043.9	1045.2
$Ca(NO_3)_2$	1042.8	1043.3	1044.7
$Sr(NO_3)_2$	1043.8	1043.5	1045.5
$Pb(NO_3)_2$	1039.2	1038.6	1038.4

Table 4 Curve-fitting results of the nitrate asymmetric stretching modes from the Raman spectra.

	0.5m			1.0m			1.7m			3.3m			Saturated		
	Position (cm^{-1})		Separation	Position (cm^{-1})		Separation	Position (cm^{-1})		Separation	Position (cm^{-1})		Separation	Position (cm^{-1})		Separation
	#1	#2		#1	#2		#1	#2		#1	#2		#1	#2	
NH_4NO_3*	1343.4	1406.7	63.3	1336.5	1405.6	69.1	1337.3	1406.3	69.0	1333.8	1403.5	69.7	1335.9	1406.2	70.3
$Mg(NO_3)_2$	1344.7	1407.9	63.2	1344.5	1410.7	66.2	1342.3	1409.1	66.8	1344.3	1412.0	67.7	1344.1	1412.6	68.5
$Ca(NO_3)_2$	1350.8	1415.2	64.4	1347.4	1415.1	67.7	1348.0	1418.9	70.9	1349.2	1426.0	76.8	1349.6	1430.9	81.3
$Sr(NO_3)_2$	1347.3	1412.2	64.9	1350.8	1415.3	64.5	1353.0	1418.1	65.1	1354.4	1421.5	67.1	1354.4	1421.5	67.1
$Pb(NO_3)_2$	1335.4	1418.3	82.9	1335.8	1423.3	87.5	1336.3	1426.7	90.4	-	-	-	1336.3	1426.7	90.4

* NH_4NO_3 has the same nitrate concentration as other nitrate solutions. The concentrations for NH_4NO_3 solutions are 1 m, 2 m, 3.4 m, 6.6 m, and saturated.

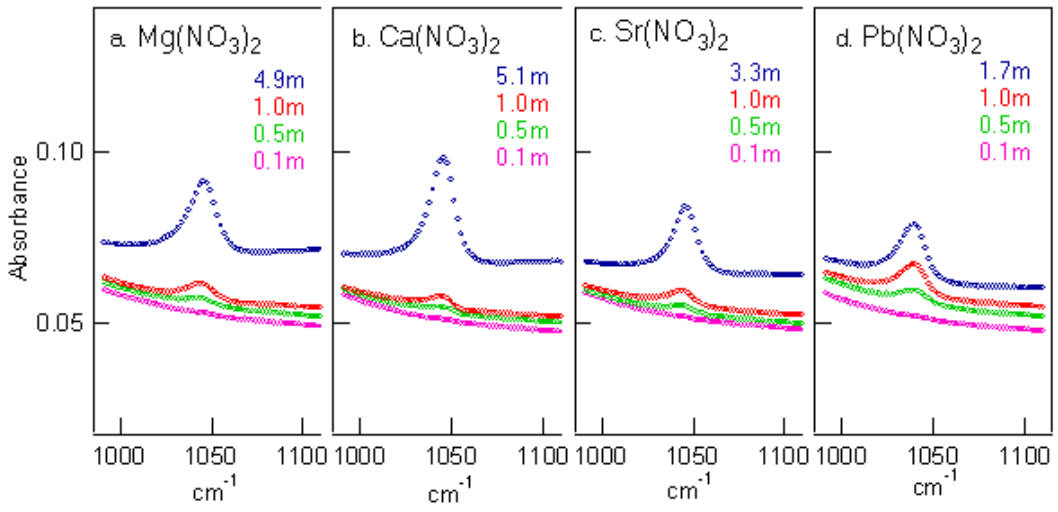

Figure 1 Infrared spectra of nitrate symmetric stretching modes: a) $Mg(NO_3)_2$ solutions; b) $Ca(NO_3)_2$ solutions; c) $Sr(NO_3)_2$ solutions; d) $Pb(NO_3)_2$ solutions.

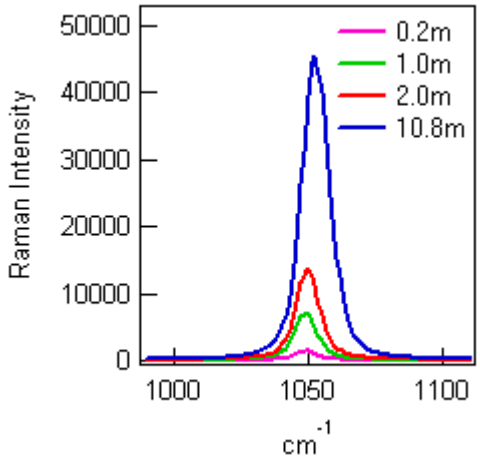

Figure 2 Raman spectra of the nitrate symmetric stretching peak from the $NaNO_3$ aqueous solutions at various concentrations.