

**Table S1** The calculated and experimental vibrational frequencies ( $\text{cm}^{-1}$ ) of “bulk” and “surface” nitrates. Only the frequencies ( $>1100 \text{ cm}^{-1}$ ) were listed.

	Substrate	Adsorbate	Structure A	Structure B	Experiment <sup>1</sup>
bulk nitrate	$\gamma\text{-Al}_2\text{O}_3(100)$	$\text{NO}_2$	1818, 1321	1737, 1236	
		$\text{NO}_3$	1561, 1198	1588, 1284	
	$\text{MgO}(001)$	$\text{NO}_2$	1680, 1259	1512, 1257	
		$\text{NO}_3$	1452, 1251	1261	
	$\text{CaO}(001)$	$\text{NO}_2$	1556, 1268	1546, 1260	1480, 1328
		$\text{NO}_3$	1374, 1343	1484, 1269	
$\text{SrO}(001)$	$\text{NO}_2$	1517, 1259	1501, 1247	1463, 1322	
	$\text{NO}_3$	1382, 1340	1468, 1272		
surface nitrate	$\text{BaO}(001)$	$\text{NO}_2$	1450, 1240	1443, 1235	1440, 1320
		$\text{NO}_3$	1409, 1317	1476, 1261	
	$\text{MgO}/\gamma\text{-Al}_2\text{O}_3(100)$	$\text{NO}_2$	1696, 1299	1585, 1227	1593, 1260
		$\text{NO}_3$	1596, 1214	1647, 1212	
	$\text{CaO}/\gamma\text{-Al}_2\text{O}_3(100)$	$\text{NO}_2$	1575, 1230	1656, 1288	1582, 1280
		$\text{NO}_3$	1607, 1210	1572, 1205	
$\text{SrO}/\gamma\text{-Al}_2\text{O}_3(100)$	$\text{NO}_2$	1576, 1231	1634, 1282	1580, 1287	
	$\text{NO}_3$	1589, 1220	1554, 1207		
$\text{BaO}/\gamma\text{-Al}_2\text{O}_3(100)$	$\text{NO}_2$	1565, 1232	1600, 1275	1577, 1310	
	$\text{NO}_3$	1574, 1219	1545, 1207		

**Table S2** The calculated and experimental vibrational frequencies ( $\text{cm}^{-1}$ ) of cubic bulk AE nitrates.

Bulk Nitrate	Calculations	Experiments
$\text{Mg}(\text{NO}_3)_2$	1463, 1430, 1426, 1398, 1380, 1364, 1096, 767, 732	1467, 1376, 1328, 1070, 1063, 1049, 748, 732 <sup>a</sup>
$\text{Ca}(\text{NO}_3)_2$	1432, 1423, 1413, 1406, 1372, 1362, 1064, 780, 720	1488, 1455, 1360, 813, 743 <sup>b</sup>
$\text{Sr}(\text{NO}_3)_2$	1420, 1414, 1406, 1395, 1365, 1354, 1051, 780, 715	1477, 1439, 1360, 1055, 815, 738 <sup>b</sup>
$\text{Ba}(\text{NO}_3)_2$	1398, 1396, 1387, 1380, 1354, 1344, 1043, 782, 710	1462, 1415, 1345, 818, 730 <sup>b</sup>

(a) Experimental data from reference<sup>2</sup>. The frequencies of  $\text{Mg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  was used for comparison.

(b) Experimental data from reference<sup>3</sup>

1. C. Verrier, J. H. Kwak, D. H. Kim, C. H. F. Peden and J. Szanyi, *Catal. Today*, 2008, **136**, 121-127.
2. X. H. Li, L. J. Zhao, J. L. Dong, H. S. Xiao and Y. H. Zhang, *J. Phys. Chem. B*, 2008, **112**, 5032-5038.
3. M. H. Brooker and J. B. Bates, *Spectroc. Acta Pt. A-Molec. Biomolec. Spectr.*, 1973, **A 29**, 439-452.