

Supporting information: Operando Potassium K-edge X-ray Absorption Spectroscopy, Investigating Potassium Catalysts during Soot Oxidation

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Scheme 1. In situ soft edge reactor

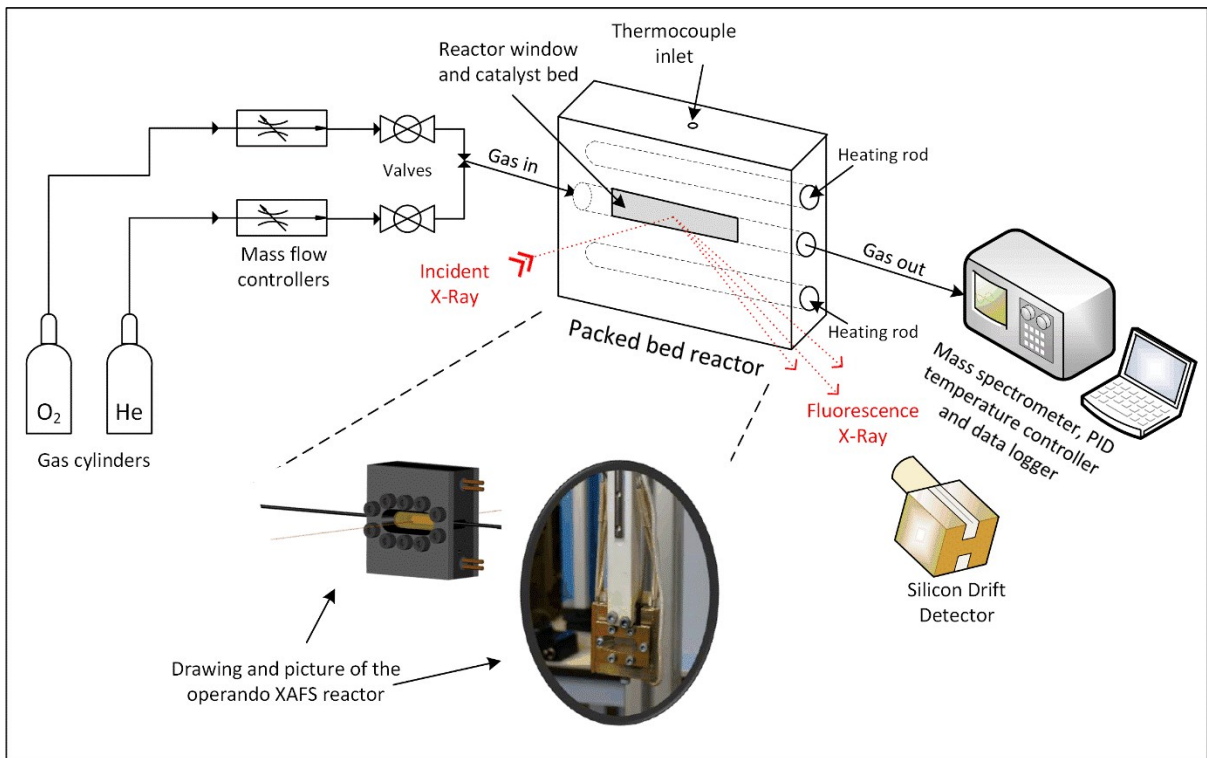


Figure 1. XRD patterns of catalysts before and after soot oxidation. (a) α -Al₂O₃, (b) α -Al₂O₃ after soot oxidation, (c) K/ α -Al₂O₃, (d) K/ α -Al₂O₃ after soot oxidation. Patterns of (b) and (d) magnified x5 for ease of comparison with fresh materials. Labelled (hkl) values for α -Al₂O₃, (●) KHCO₃, (|) K₂CO₃.xH₂O

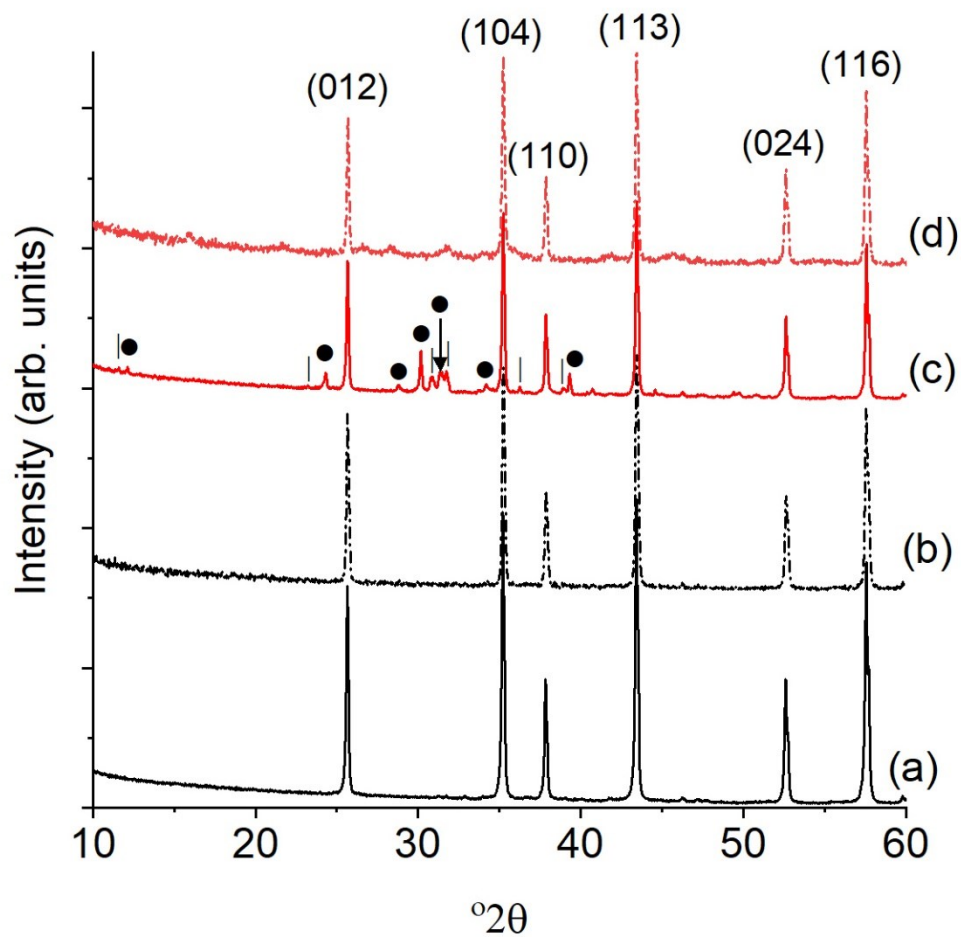


Figure 2. K (2p) and C (1s) XPS spectra for (a) K/ α -Al₂O₃ and (b) K/ α -Al₂O₃ after soot oxidation. (blue) K 2p_{1/2} and K 2p_{3/2} peak fitting, (red) C 1s peak fitting and (green) baseline.

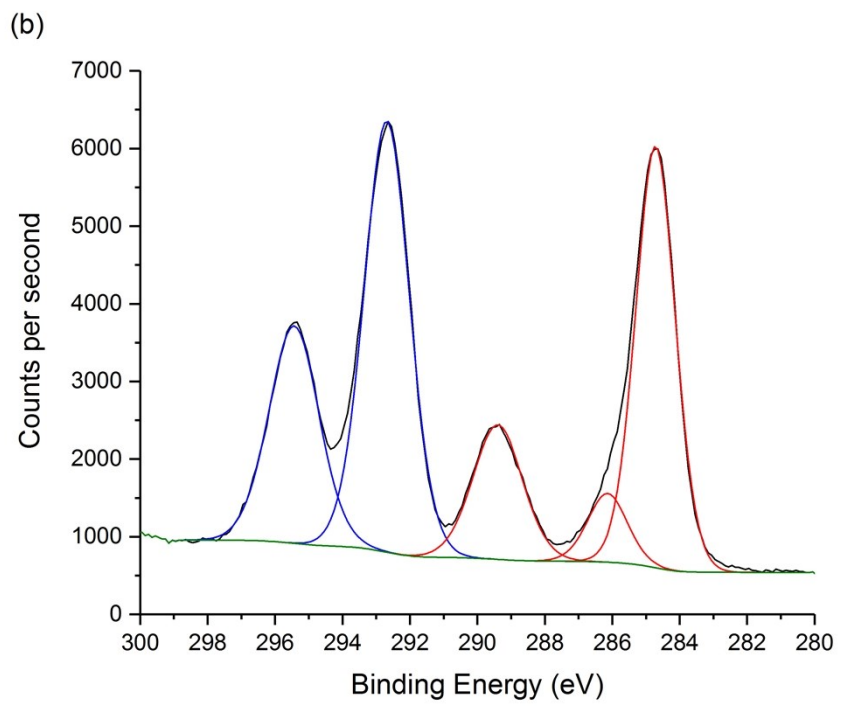
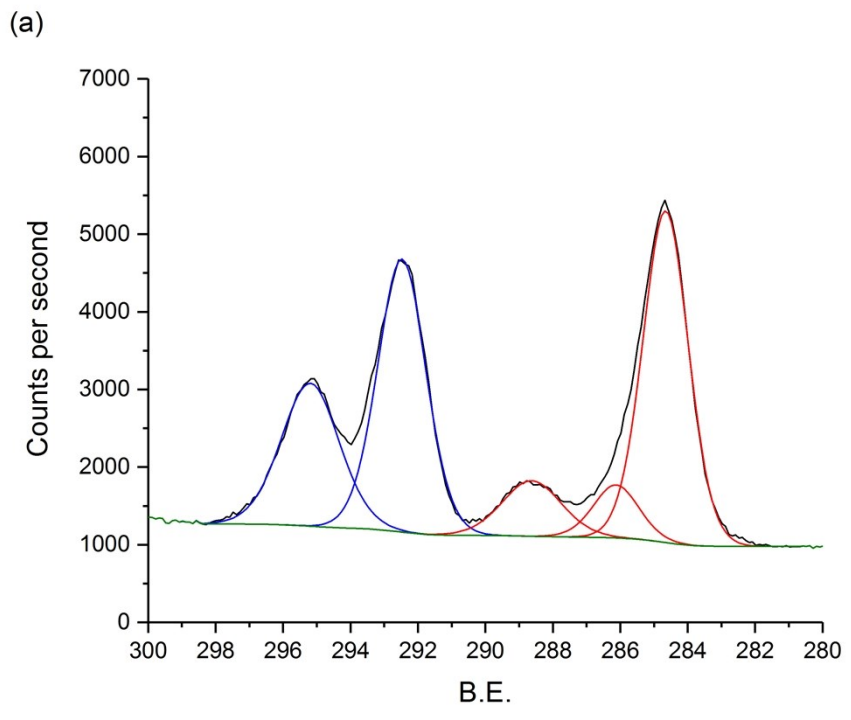
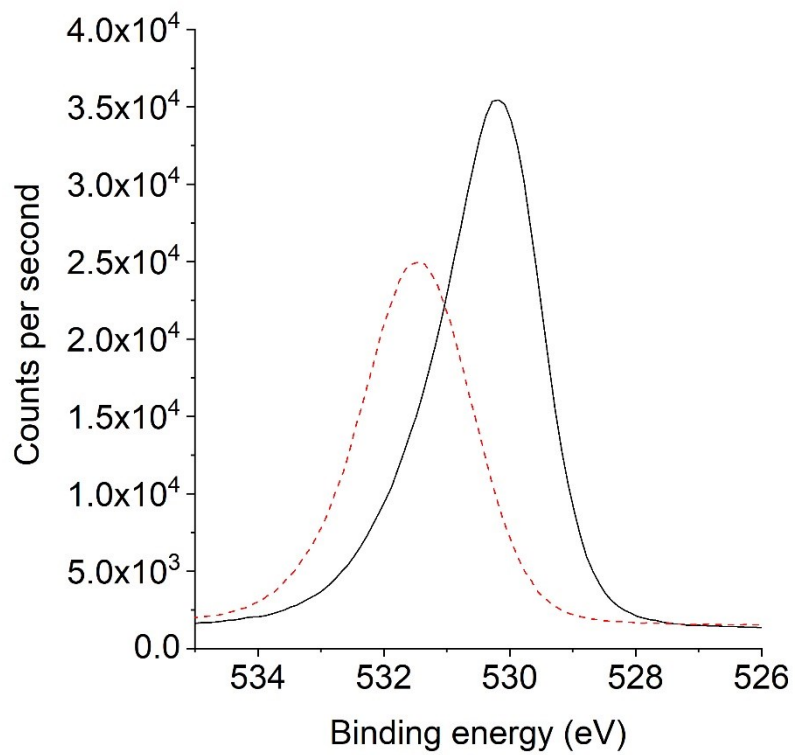


Figure 3. O (1s) XPS spectra for K/ α -Al₂O₃ and K/ α -Al₂O₃ after soot oxidation. K/ α -Al₂O₃ (black line and K/ α -Al₂O₃ after soot oxidation (dashed red line).



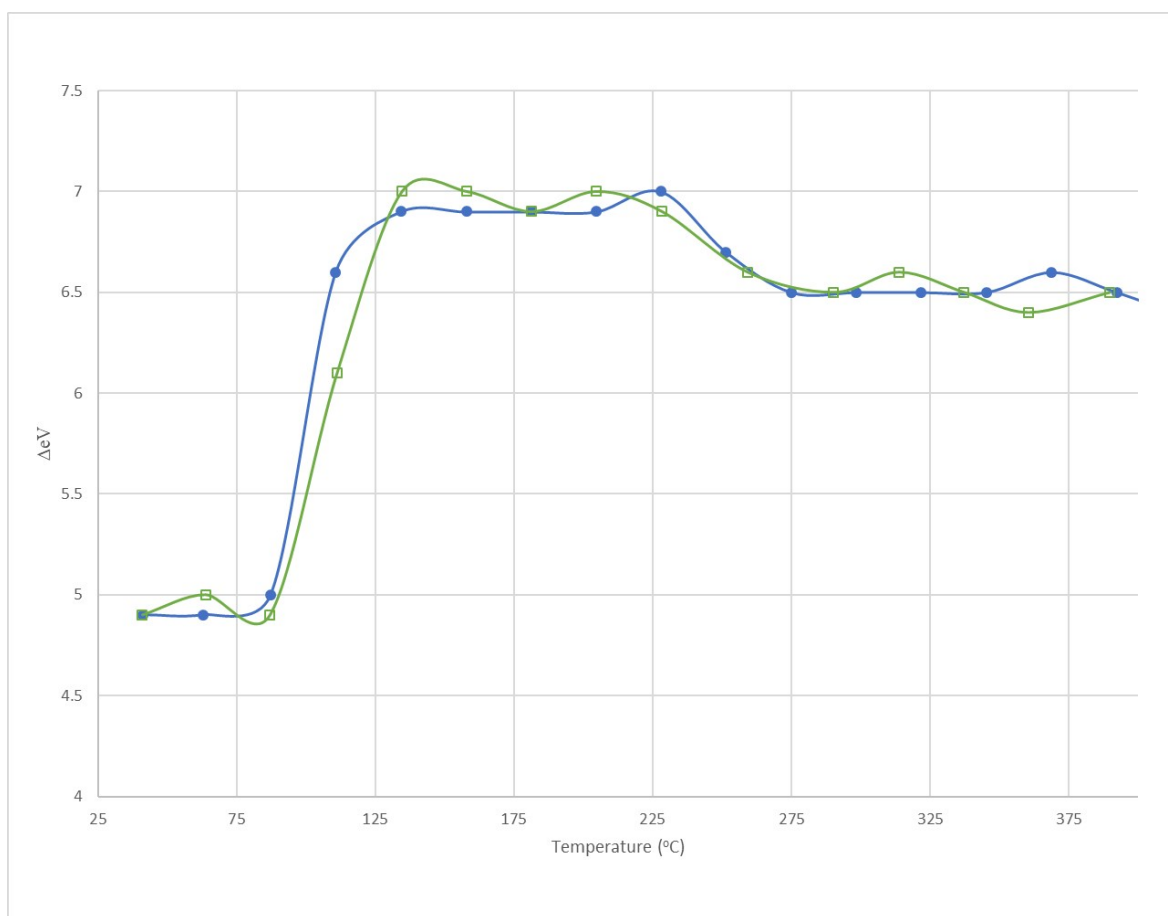


Figure 4. Comparison of ΔCB for repeat runs of XANES K/ α - Al_2O_3 in the presence of soot

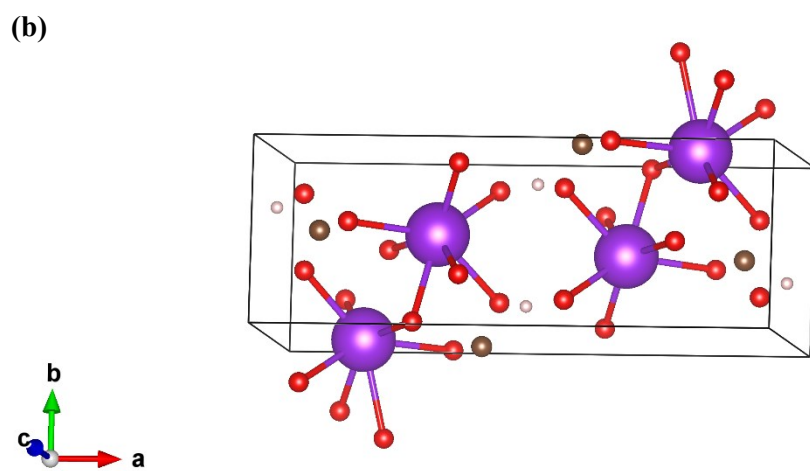
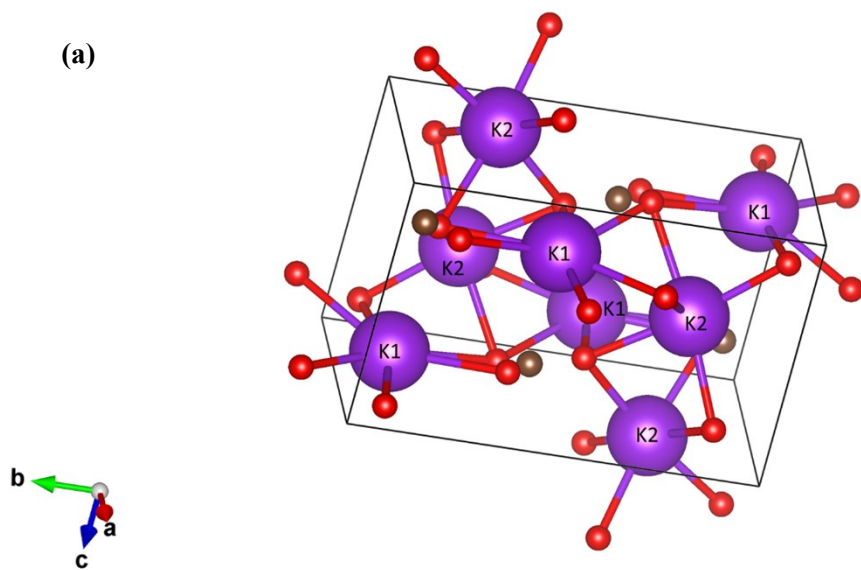


Figure 5. Structural images from VESTA (a) K_2CO_3 (ICSD_CollCode66943) showing the 2 potassium environments (b) $KHCO_3$ (ICSD_CollCode2074)

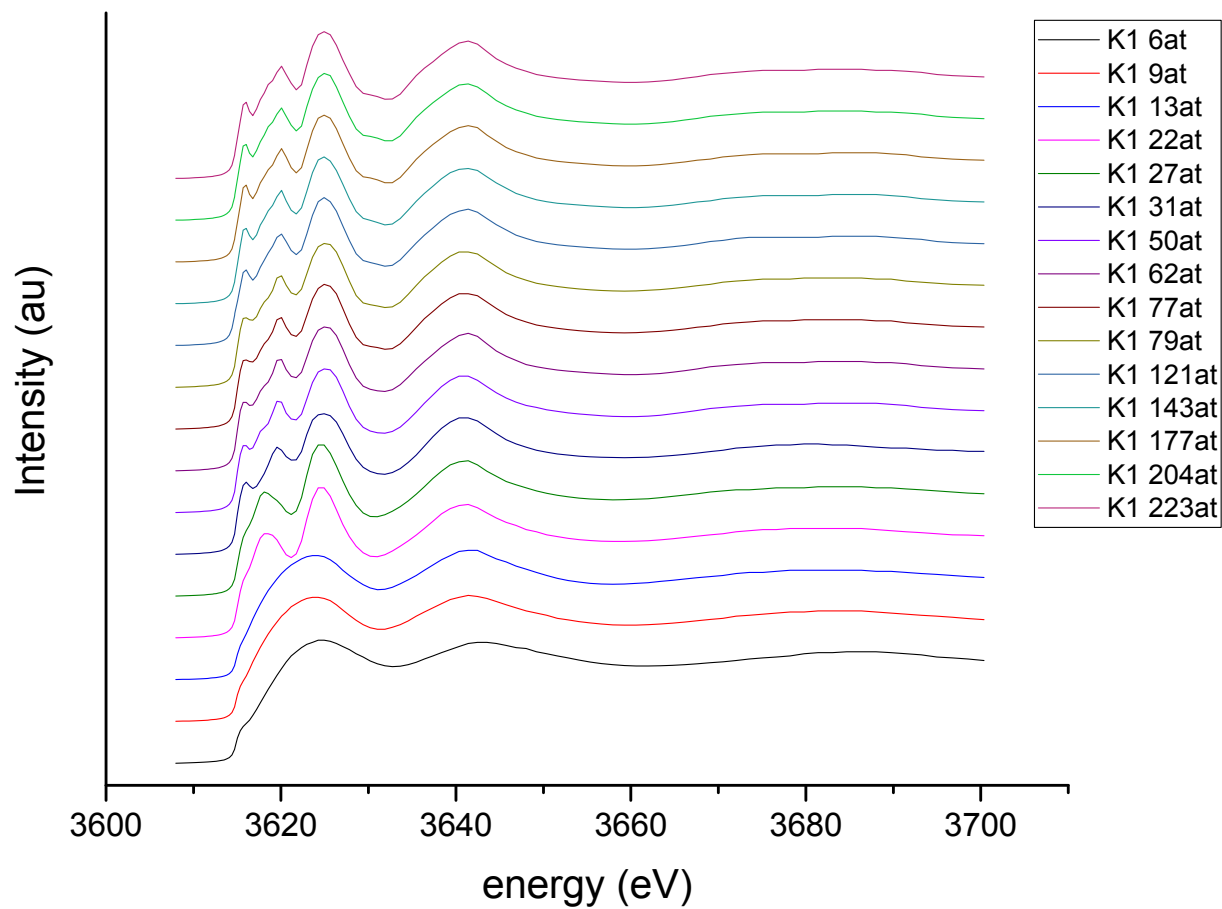


Figure 6. K_2CO_3 K1 cluster size effects ranging from 6 atoms to 223 atoms

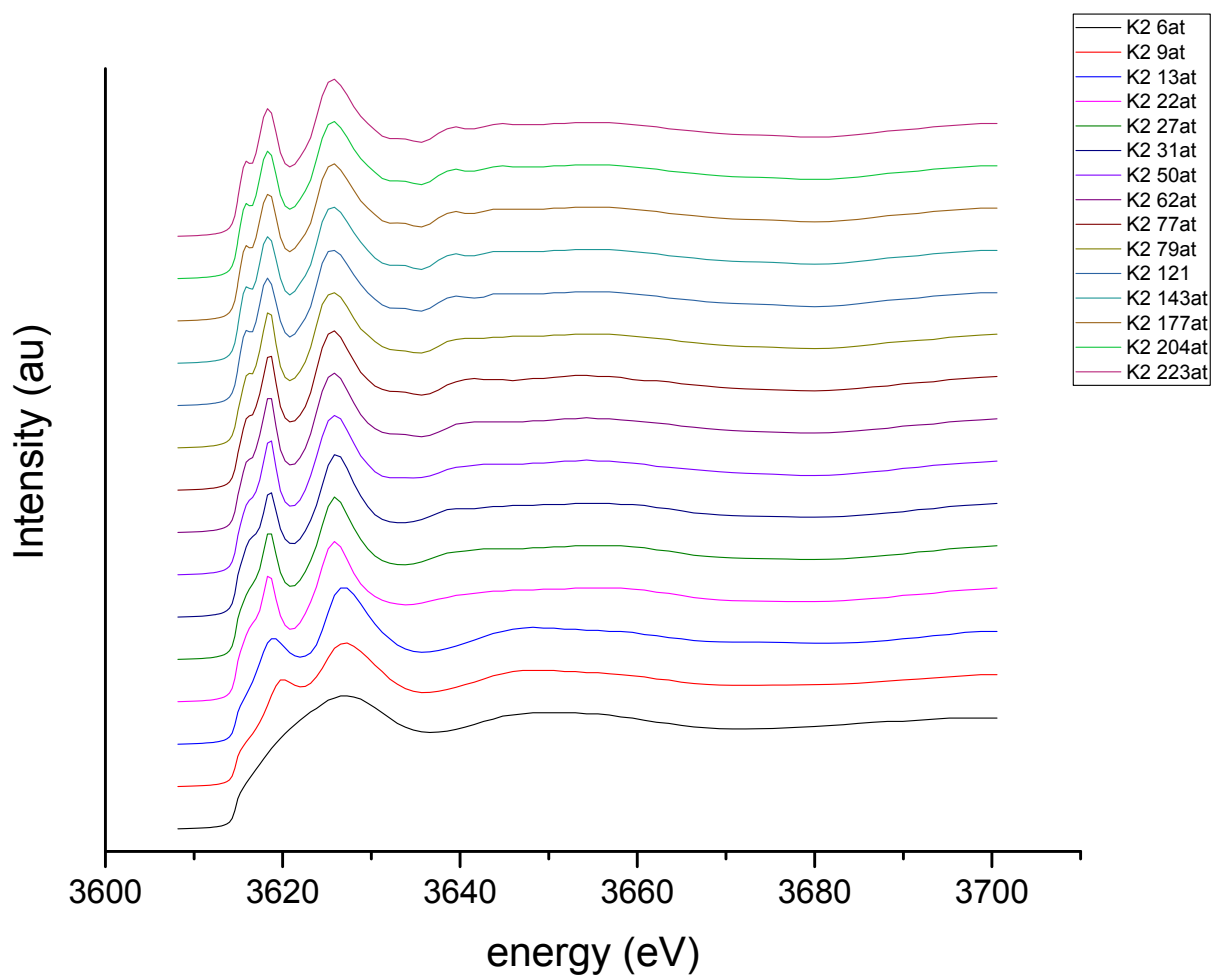


Figure 7. K_2CO_3 K2 cluster size effects ranging from 6 atoms to 223 atoms

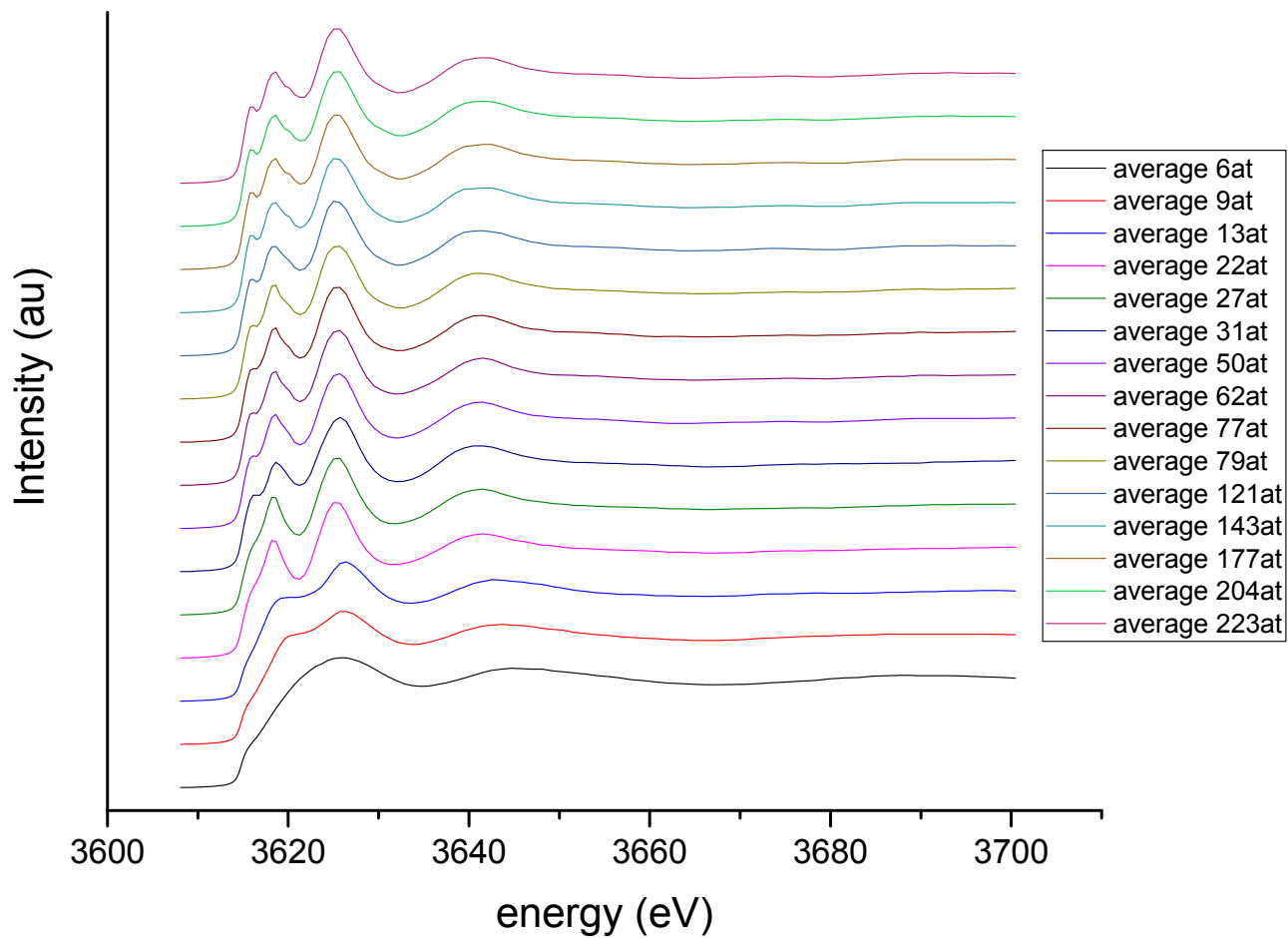


Figure 8. Sum of K_2CO_3 K1 and K2 cluster size effects ranging from 6 atoms to 223 atoms.

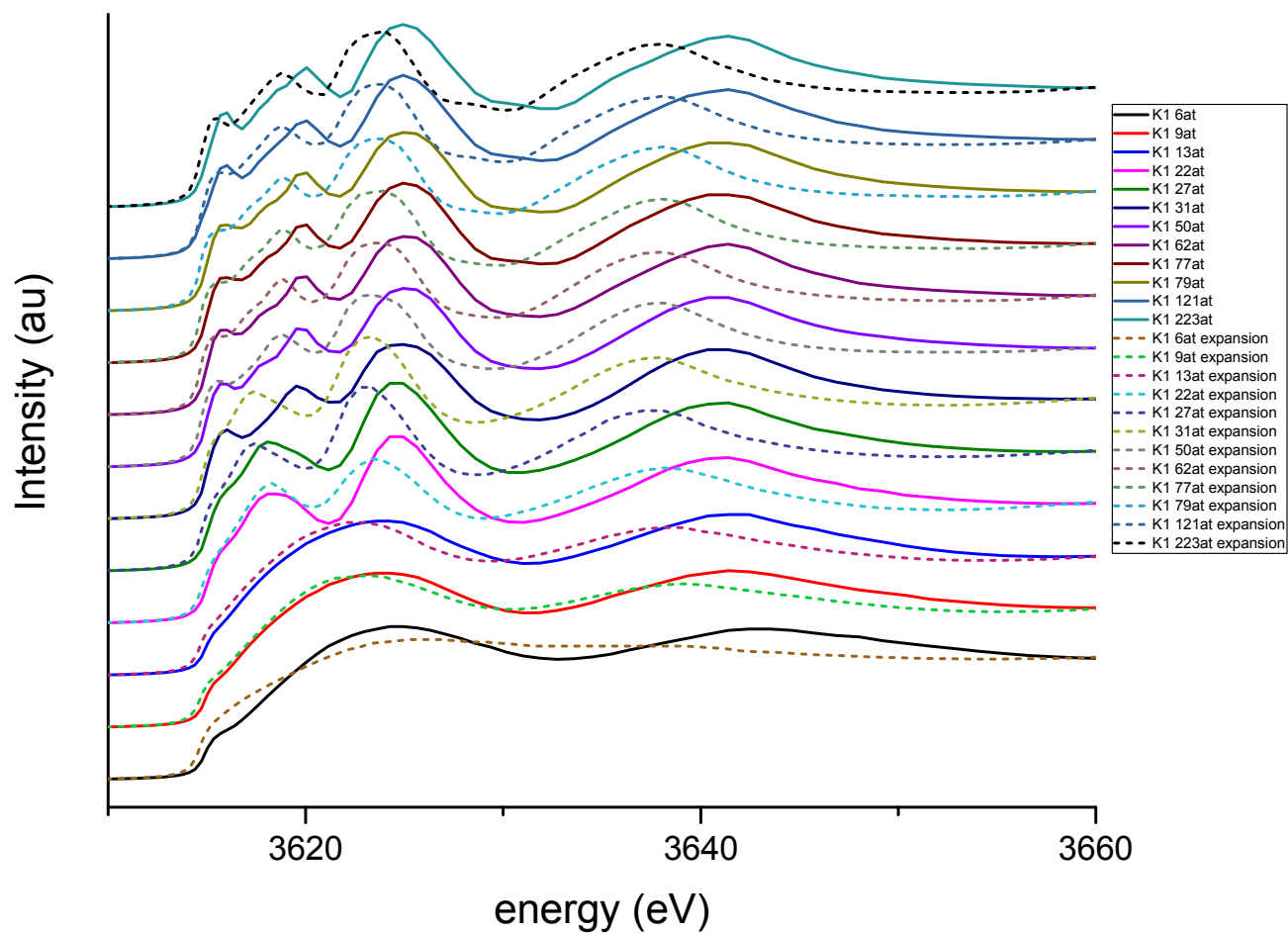


Figure 9. K_2CO_3 K1 clusters compared with 5 percent expansion of bond lengths

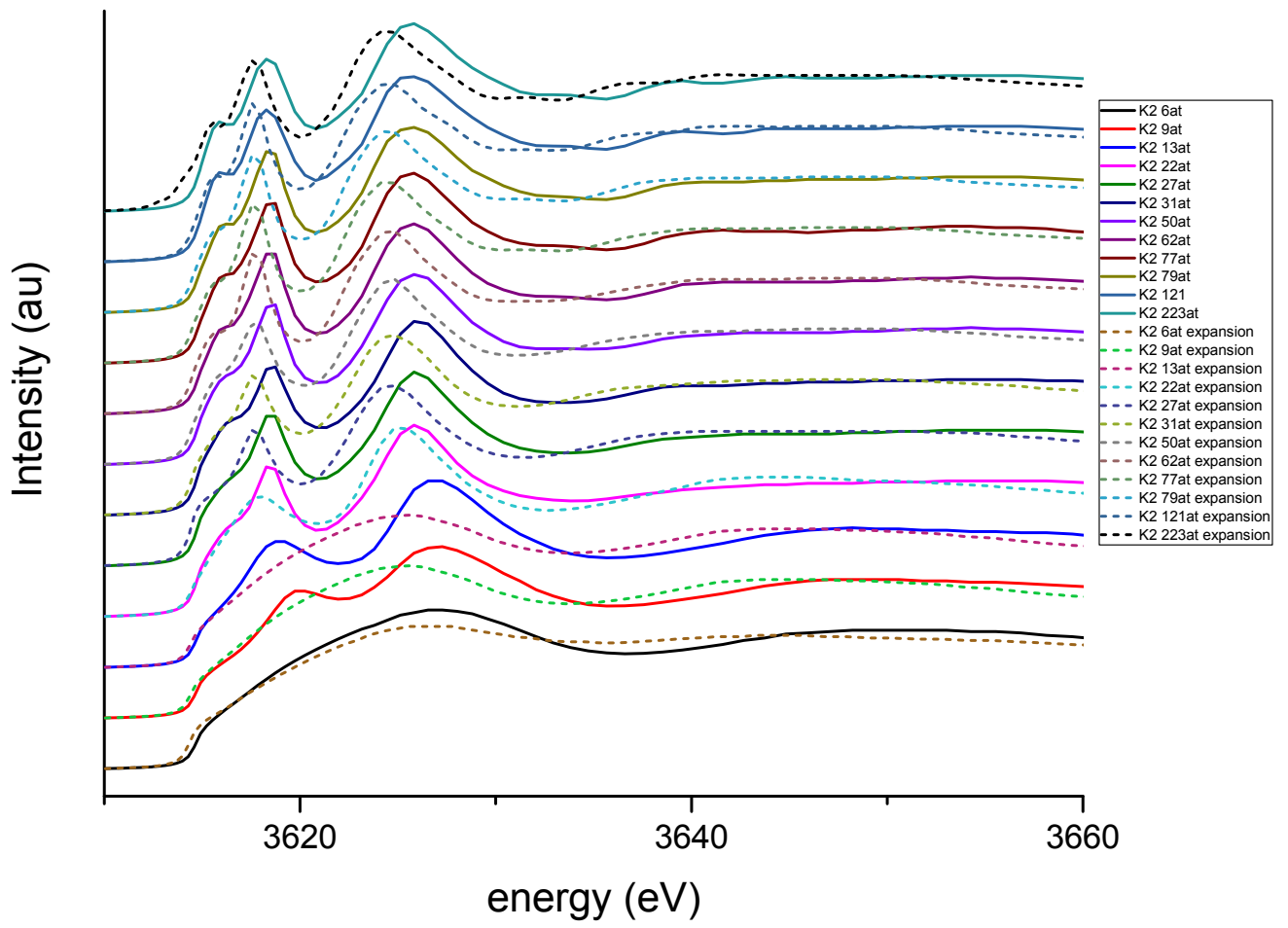


Figure 10. K_2CO_3 K2 clusters compared with 5 percent expansion of bond lengths

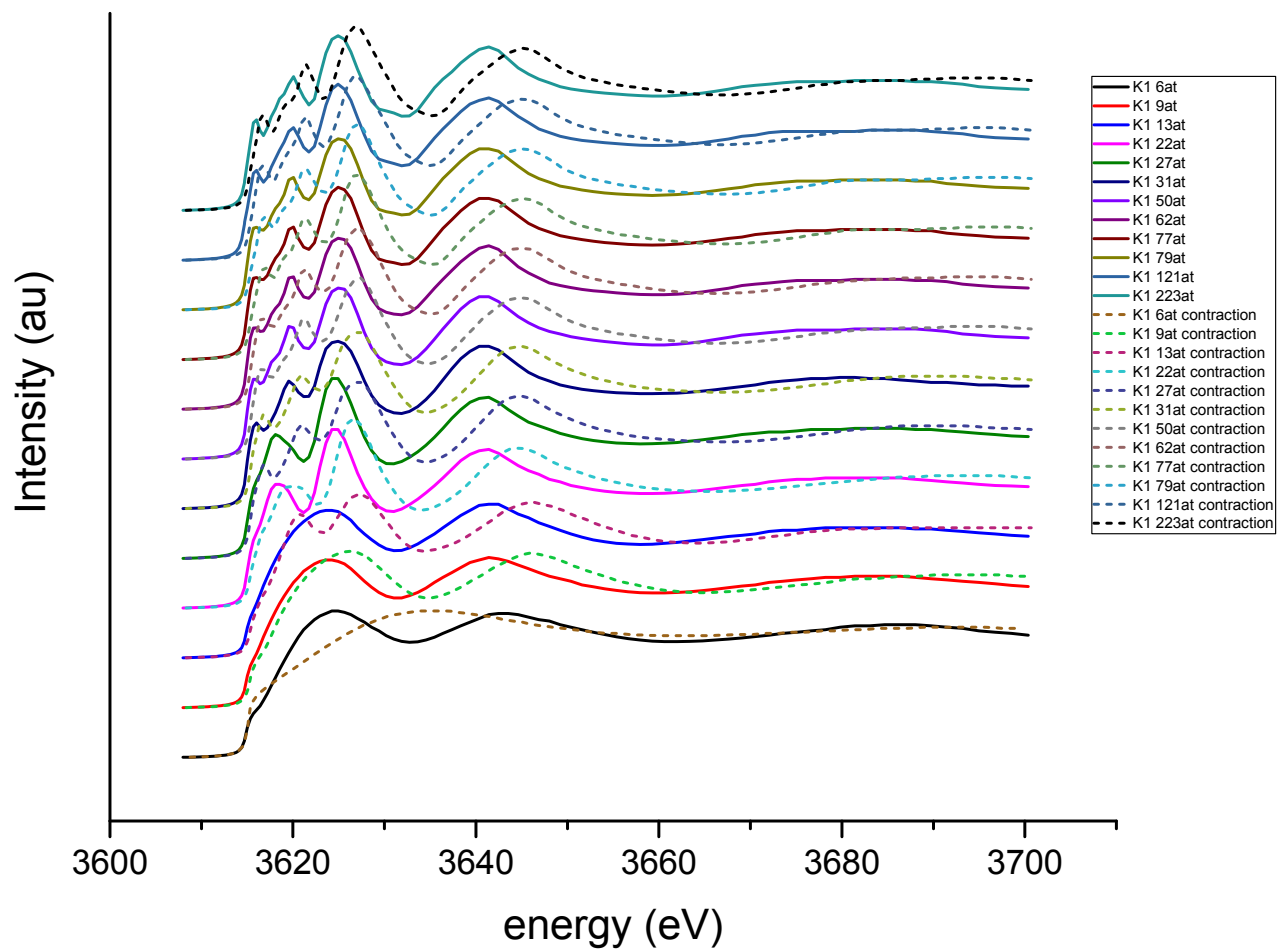


Figure 11. K_2CO_3 K1 clusters compared with 5 percent contraction of bond lengths

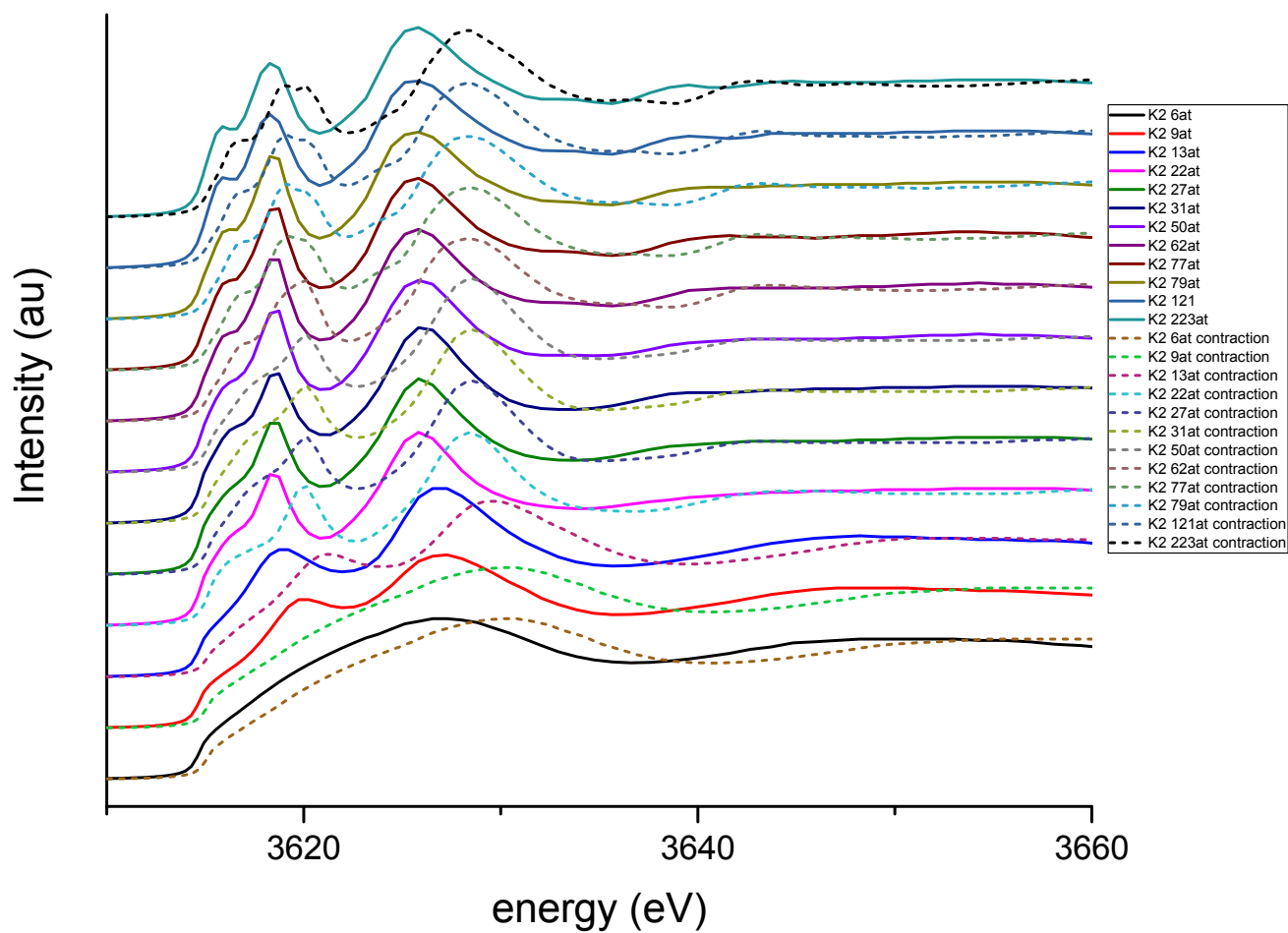


Figure 12. K_2CO_3 K2 clusters compared with 5 percent contraction of bond lengths

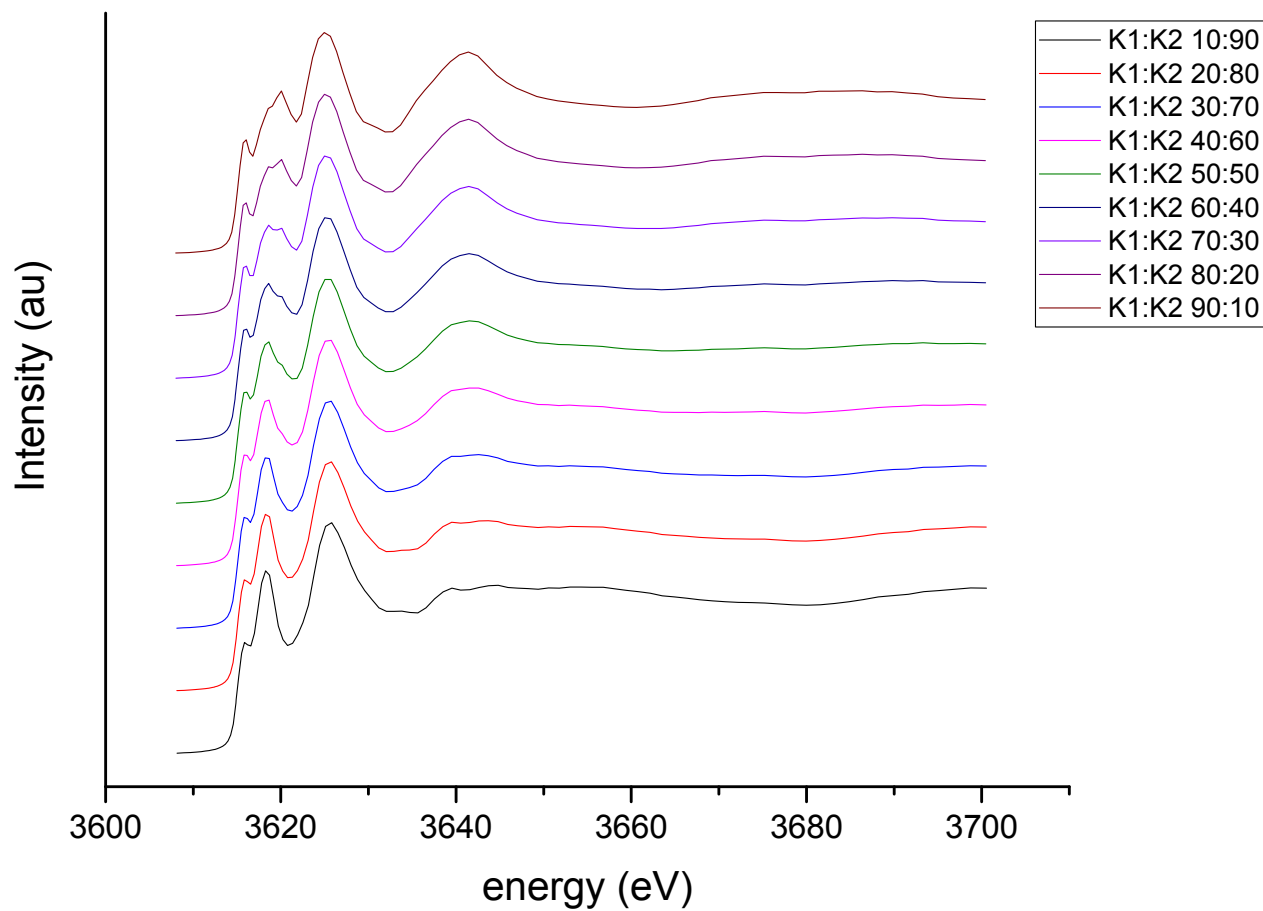


Figure 13. Changing ratios for the contribution of K1 and K2 in K_2CO_3

Simulation	Band A (1s →3d)	Band B (1s →4p)	Band C (1s →CR)	Band C - B
K2CO3 K1				
6 atoms	-	-	3620.7	-
22 atoms	3611.8	3614.3	3620.6	6.3
121 atoms	3612.0	3616.0	3621.0	5
223 atoms	3612.0	3616.1	3621.0	4.9
K2CO3 K2				
6 atoms	-	-	3623.0	-
22 atoms	3612.3	3614.3	3621.9	7.6
121 atoms	3611.9	3614.3	3621.7	7.4
223 atoms	3611.9	3614.3	3621.8	7.5
K2CO3 sum of K1 & K2				
6 atoms	-	-	3621.8	-
22 atoms	3611.9	3614.3	3621.4	7.1
121 atoms	3612.0	3614.5	3621.2	6.7
223 atoms	3611.9	3614.6	3621.4	6.8
KHCO3				
6 atoms	-	-	3622.2	-
22 atoms	-	3615.3	3621.4	6.1
50 atoms	3612.4	3615.2	3620.1 + 3623.3	4.9 + 8.1
K2CO3 K1 expansion				
6 atoms	-	-	3621.8	-
22 atoms	3611.5	3614.2	3619.3	5.1
121 atoms	3611.4	3614.7	3619.5	4.8
223 atoms	3611.3	3614.8	3619.4	4.6
K2CO3 K2 expansion				
6 atoms	-	-	3622.7	-
22 atoms	-	3613.9	3620.9	7.0
121 atoms	3611.6	3613.5	3620.5	7.0
223 atoms	3611.6	3613.5	3620.4	6.9
K2CO3 K1 Contraction				
6 atoms	-	-	3629.5	-
22 atoms	3612.8	3616.4	3622.7	6.3

121 atoms	3612.7	3617.5	3622.8	5.3
223 atoms	3612.7	3617.5	3622.8	5.3
K2CO3 K2 Contraction				
6 atoms	-	-	3626.2	-
22 atoms	3612.0	3616.1	3624.4	8.3
121 atoms	3612.6	3616.1	3624.3	8.2
223 atoms	3612.5	3616.1	3624.3	8.2
K2CO3 sum of K1 & K2 expansion				
6 atoms	-	-	3622.1	-
22 atoms	3611.5	3614.2	3620.7	6.5
121 atoms	3611.5	3613.6	3620.2	6.6
223 atoms	3611.7	3613.8	3620.1	6.3
K2CO3 sum of K1 & K2 contraction				
6 atoms	-	-	3621.3	-
22 atoms	3612.4	3616.0	3623.6	7.6
121 atoms	3612.8	3616.2	3623.5	7.3
223 atoms	3612.9	3616.1	3623.5	7.4
K2CO3 changing ratios of K1 and K2 223 atoms				
K1:K2 90:10	3611.9	3616.1	3621.0	4.9
K1:K2 80:20	3611.9	3616.0	3621.0	5.0
K1:K2 70:30	3611.9	3615.4	3621.2	5.8
K1:K2 60:40	3611.9	3614.6	3621.3	6.7
K1:K2 50:50	3611.9	3614.6	3621.4	6.8
K1:K2 40:60	3611.9	3614.5	3621.6	7.1
K1:K2 30:70	3611.9	3614.4	3621.6	7.2
K1:K2 20:80	3611.9	3614.3	3621.7	7.4
K1:K2 10:90	3611.9	3614.2	3621.7	7.5

Table 1. Peak positions for simulations of K_2CO_3 and $KHCO_3$. The peak positions are shifted by 4 eV to compare with experimental data.