Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

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

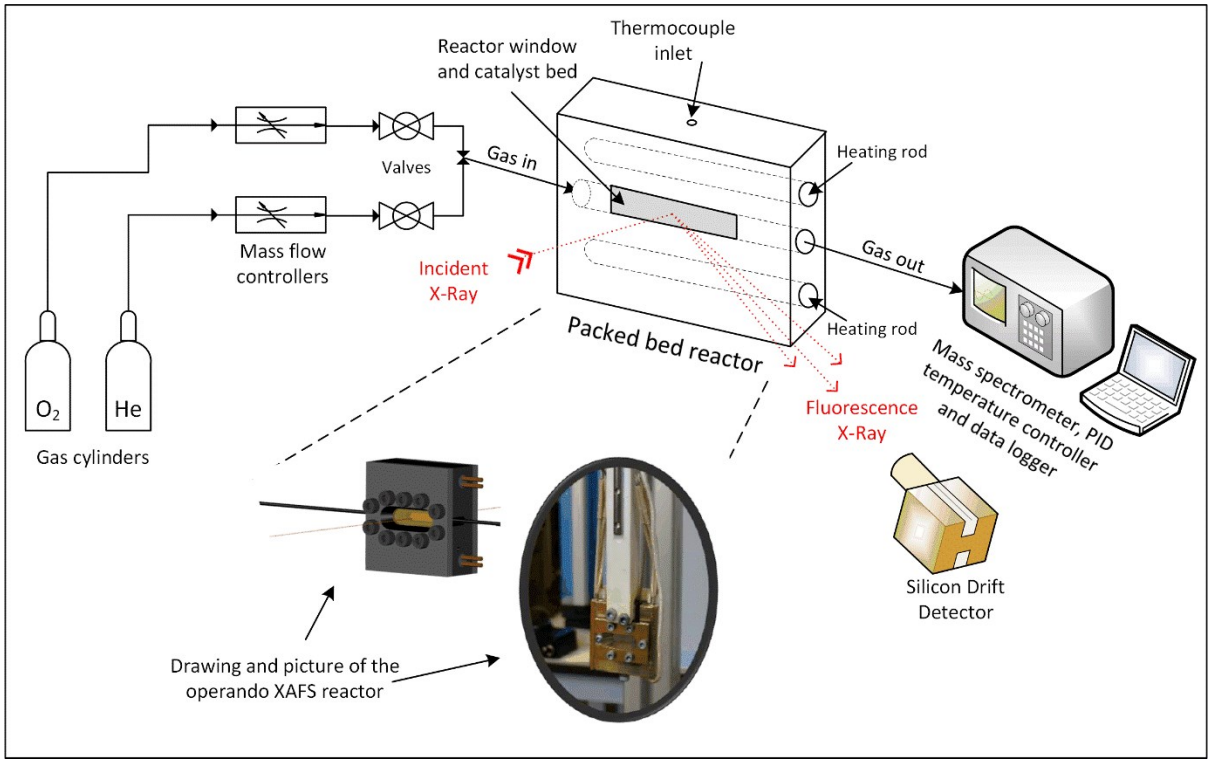


Figure 1. XRD patterns of catalysts before and after soot oxidation. (a) α-Al_2O_3, (b) α-Al_2O_3 after soot oxidation, (c) K/α-Al_2O_3, (d) K/α-Al_2O_3 after soot oxidation. Patterns of (b)and (d) magnified x5 for ease of comparison with fresh materials. Labelled (hkl) values for α-Al_2O_3, (●) $KHCO_3$, (|) $K_2CO_3.xH_2O$

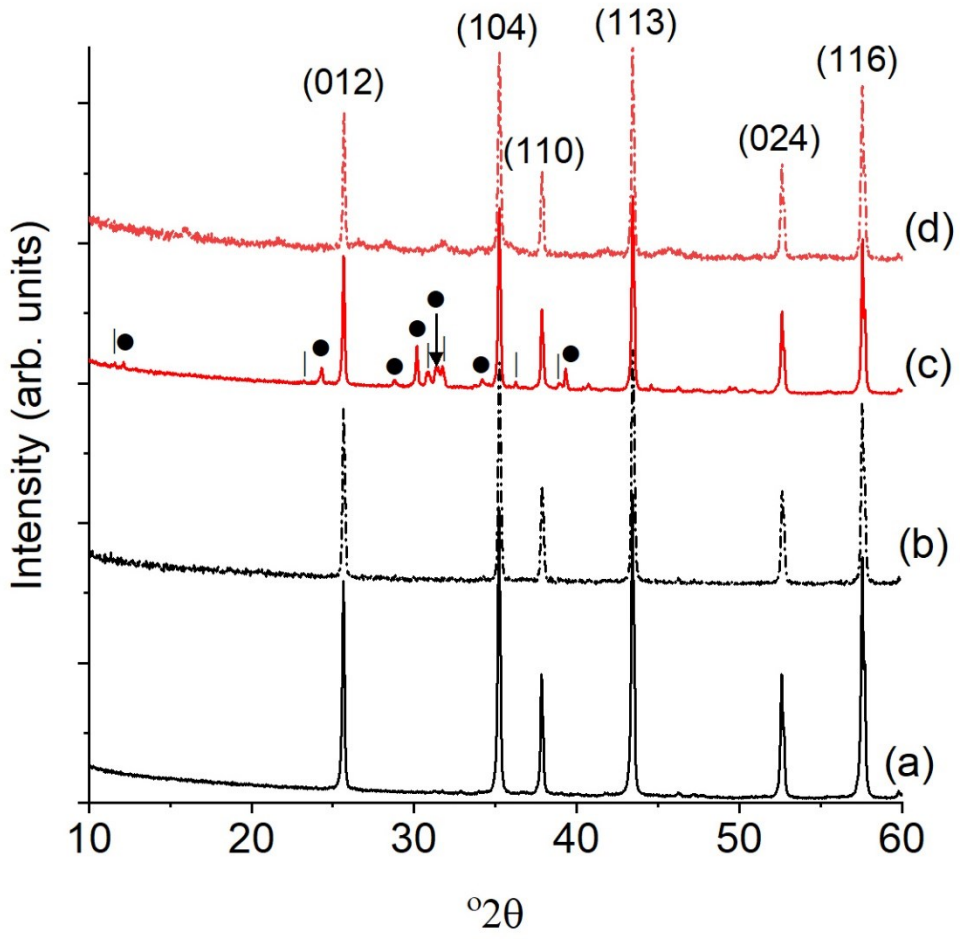


Figure 2. K (2p) and C (1s) XPS spectra for (a) K/α-Al_2O_3 and (b) K/α-Al_2O_3 after soot oxidation. (blue) K $2p_{1/2}$ and K $2p_{3/2}$ peak fitting, (red) C 1s peak fitting and (green) baseline.

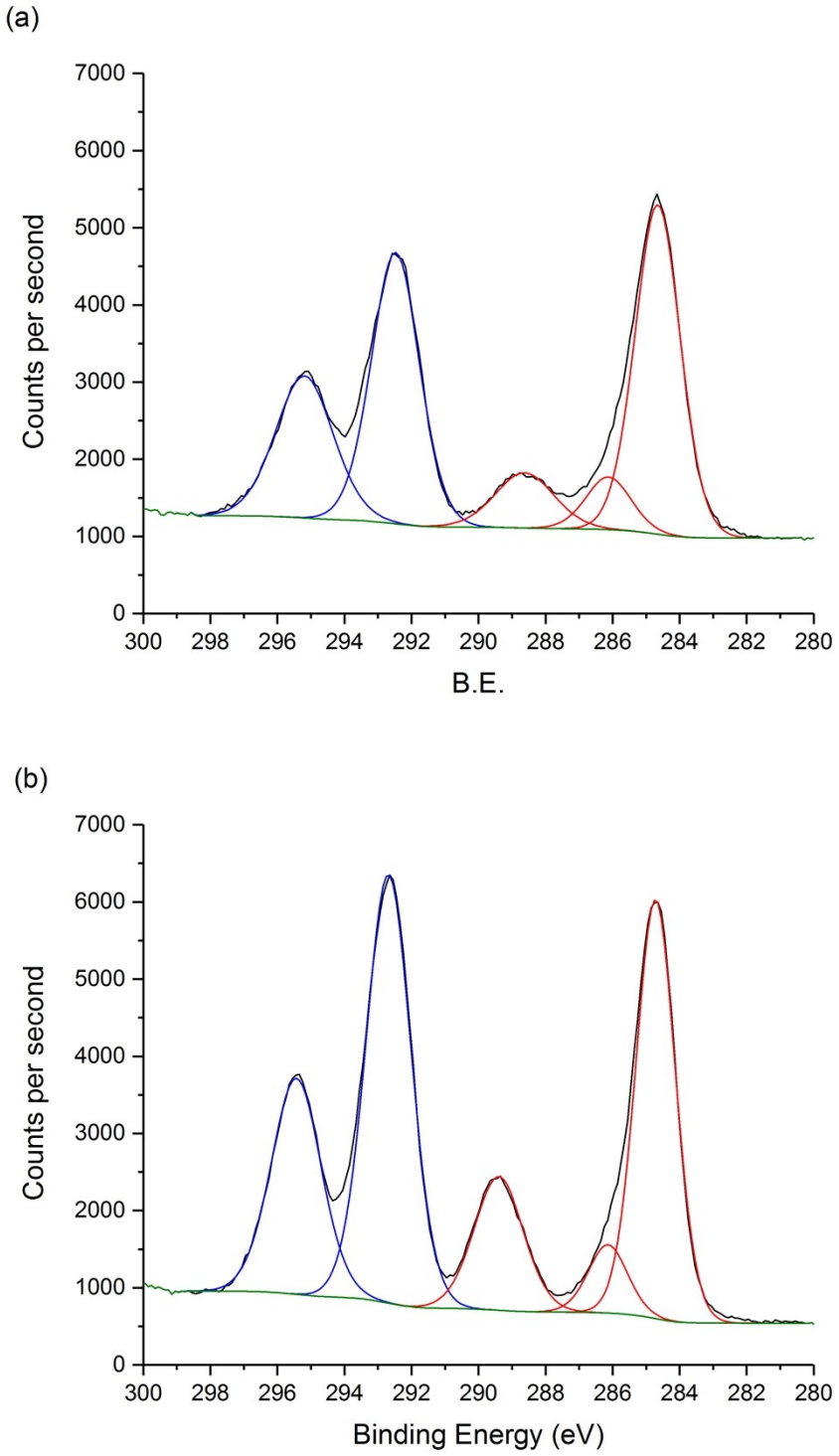
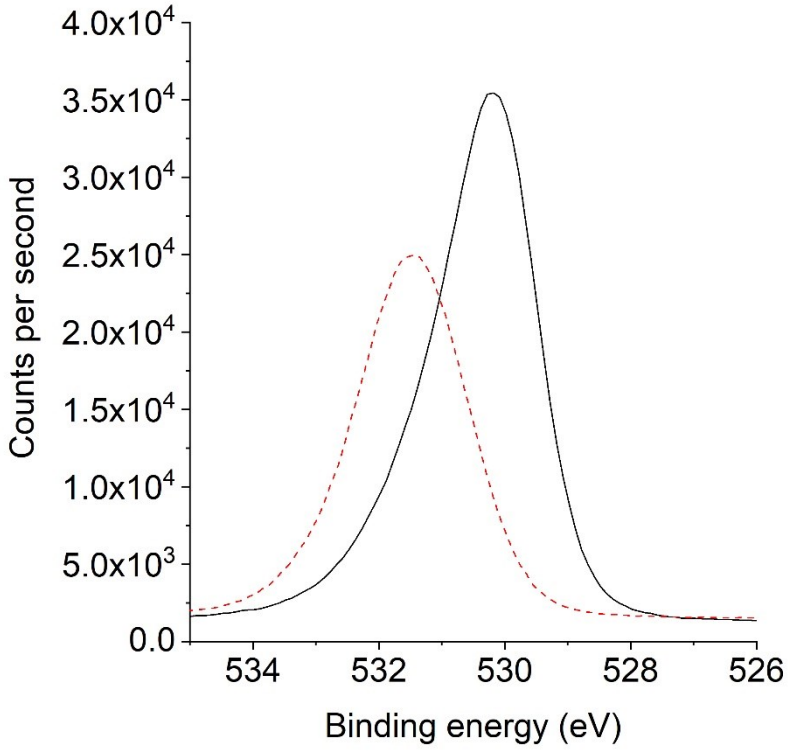


Figure 3. O (1s) XPS spectra for K/α-Al_2O_3 and K/α-Al_2O_3 after soot oxidation. K/α-Al_2O_3 **(**black line and K/α-Al_2O_3 after soot oxidation (dashed red line).



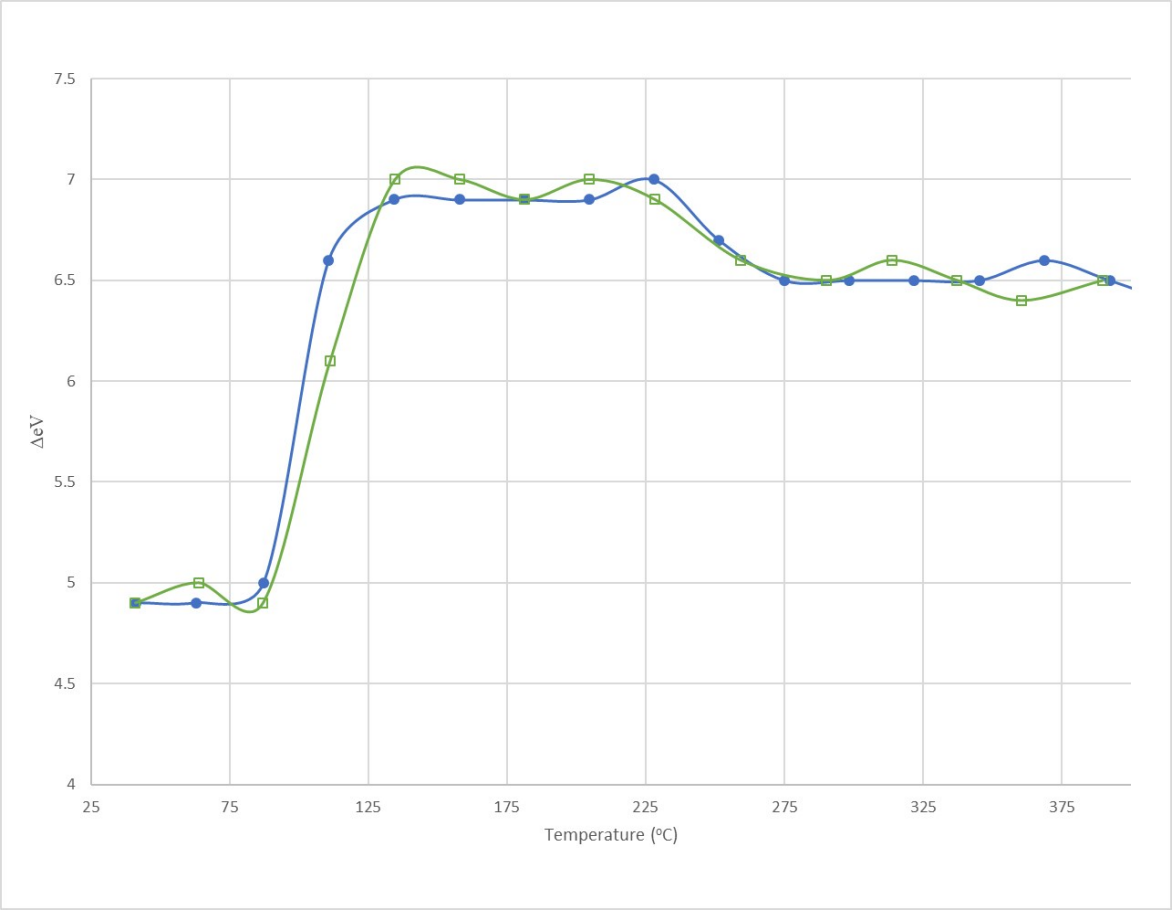


Figure 4. *Comparison of ΔCB for repeat runs of XANES K/α-Al_2O_3 in the presence of soot*

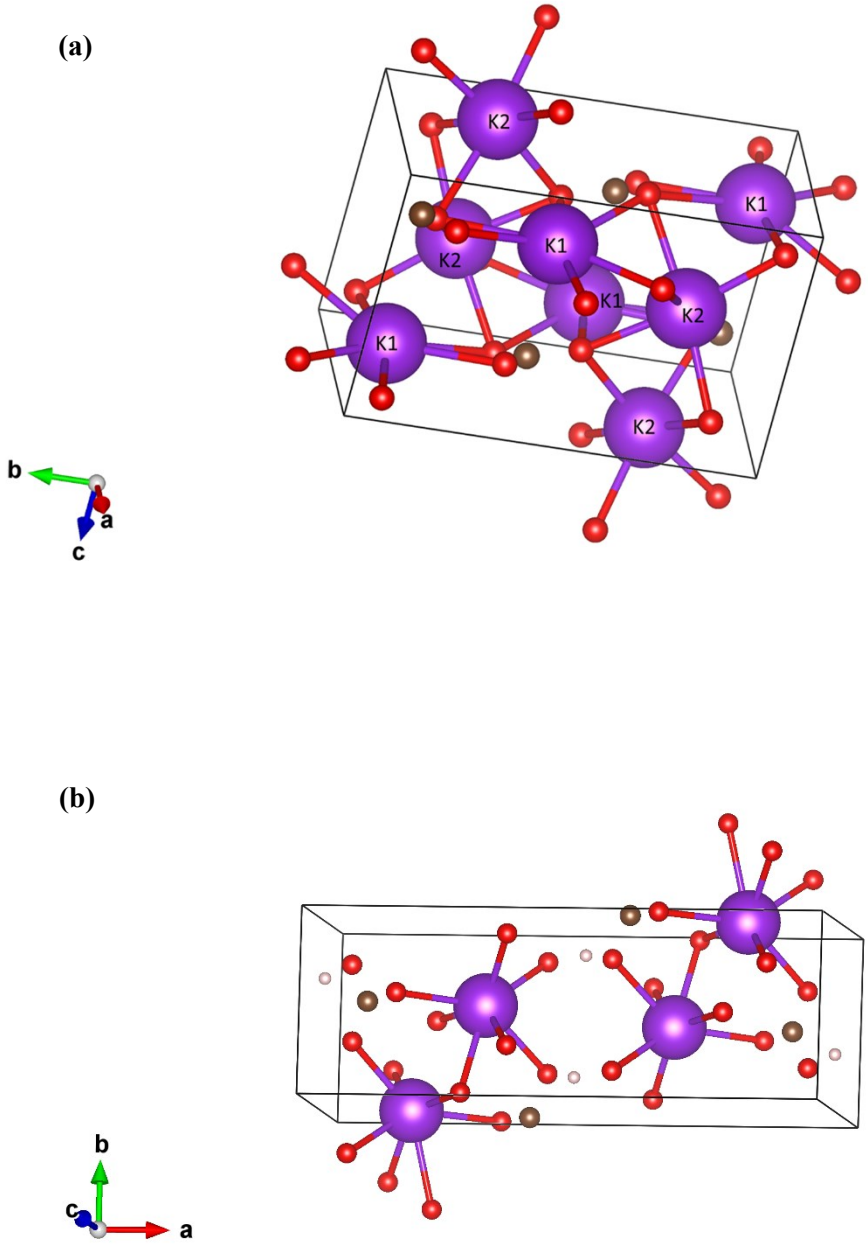


Figure 5. *Structural images from VESTA (a) K_2CO_3 (ICSD_CollCode66943) showing the 2 potassium environments (b) $KHCO_3$ (ICSD_CollCode2074)*

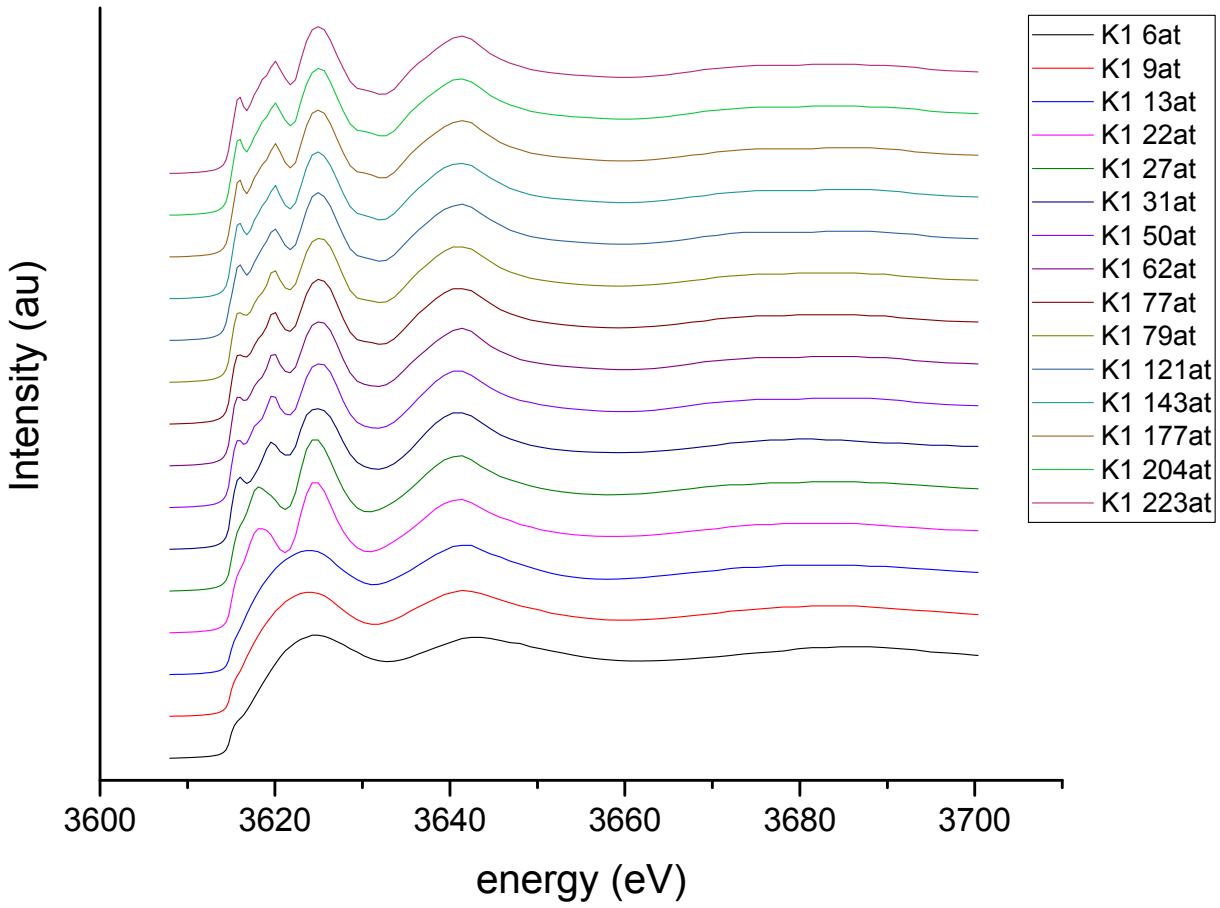


Figure 6. *K_2CO_3 K1 cluster size effects ranging from 6 atoms to 223 atoms*

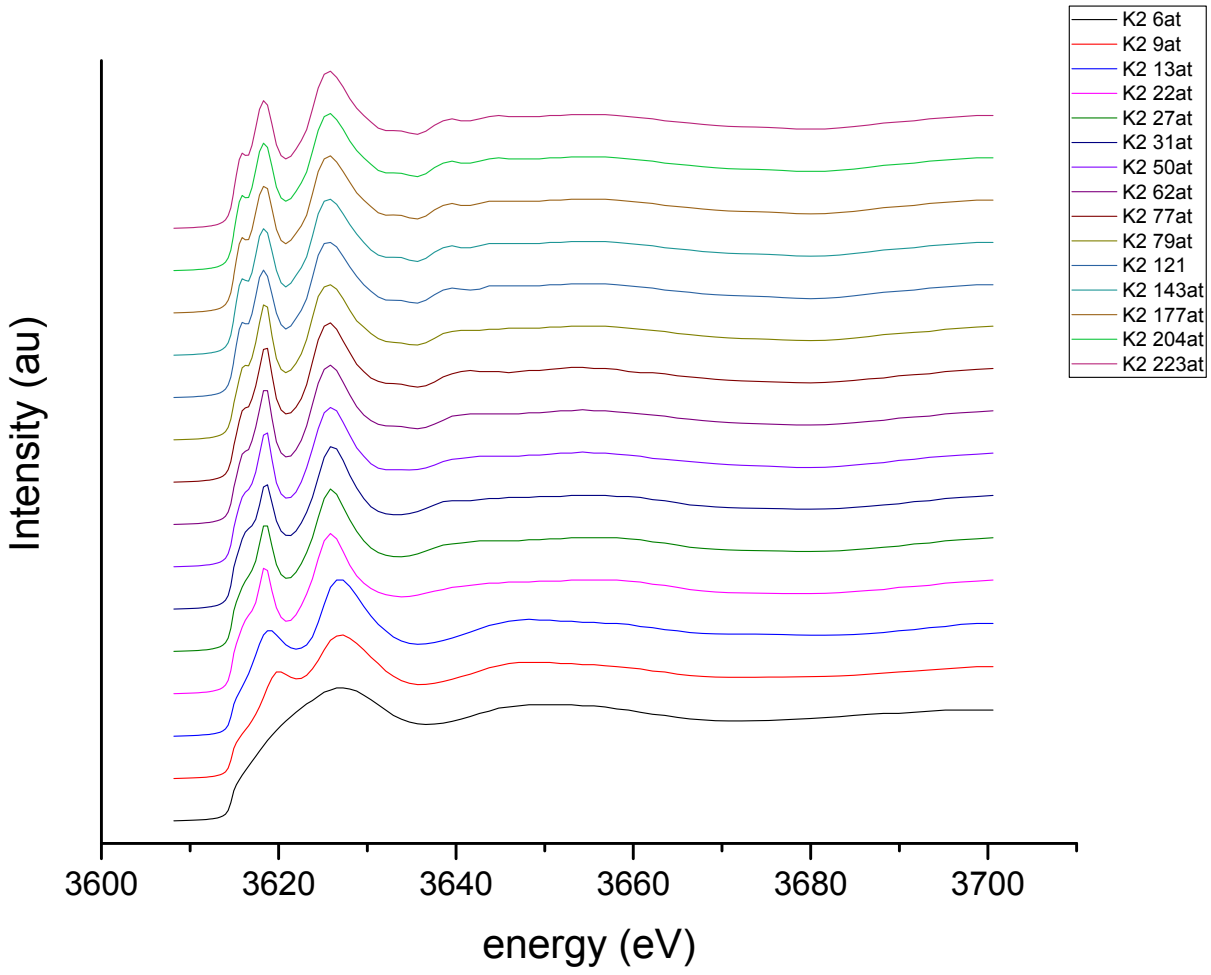


***Figure 7**. K_2CO_3 K2 cluster size effects ranging from 6 atoms to 223 atoms*

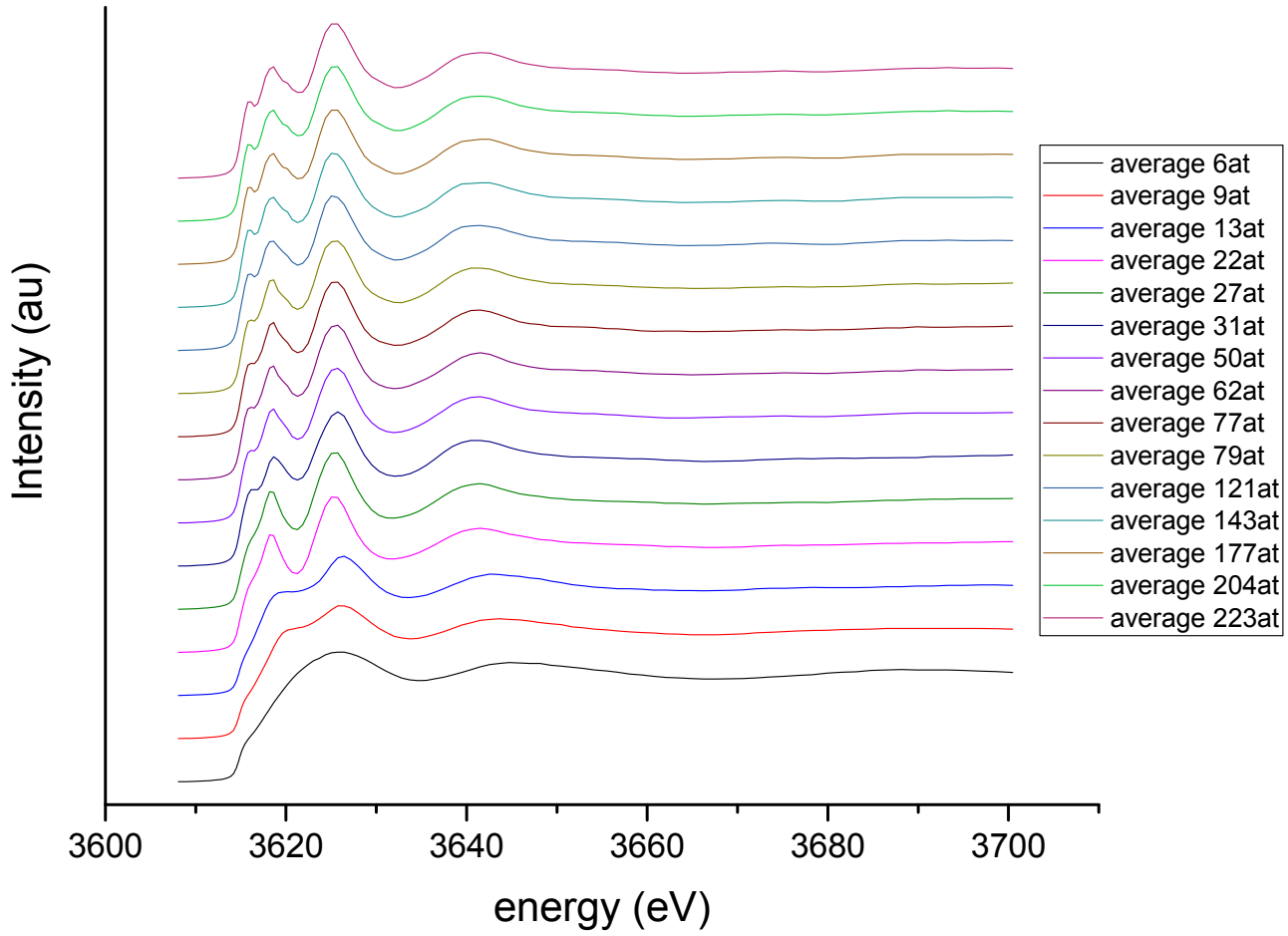


Figure 8. *Sum of K_2CO_3 K1 and K2 cluster size effects ranging from 6 atoms to 223 atoms.*

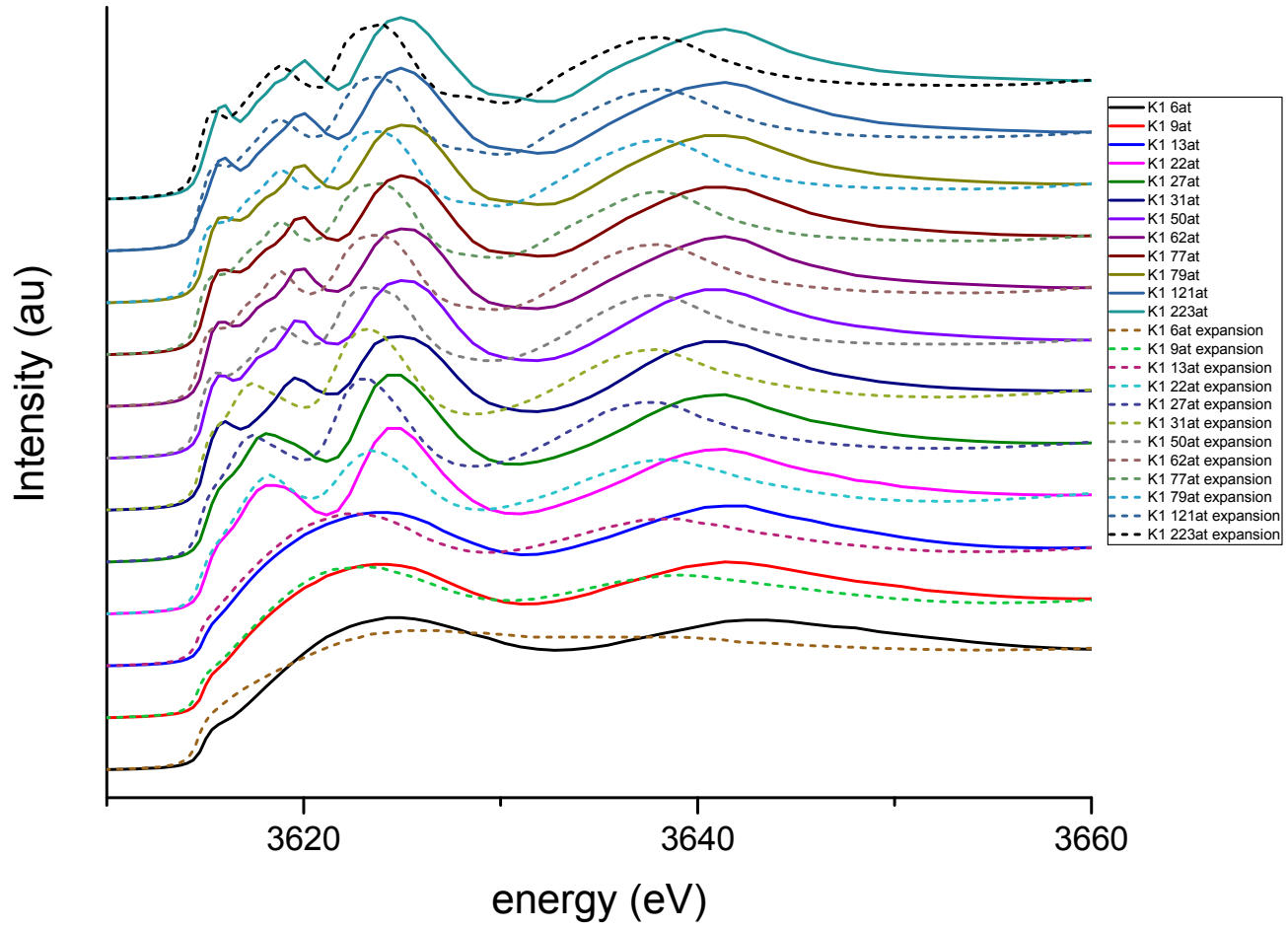


Figure 9. *K_2CO_3 K1 clusters compared with 5 percent expansion of bond lengths*

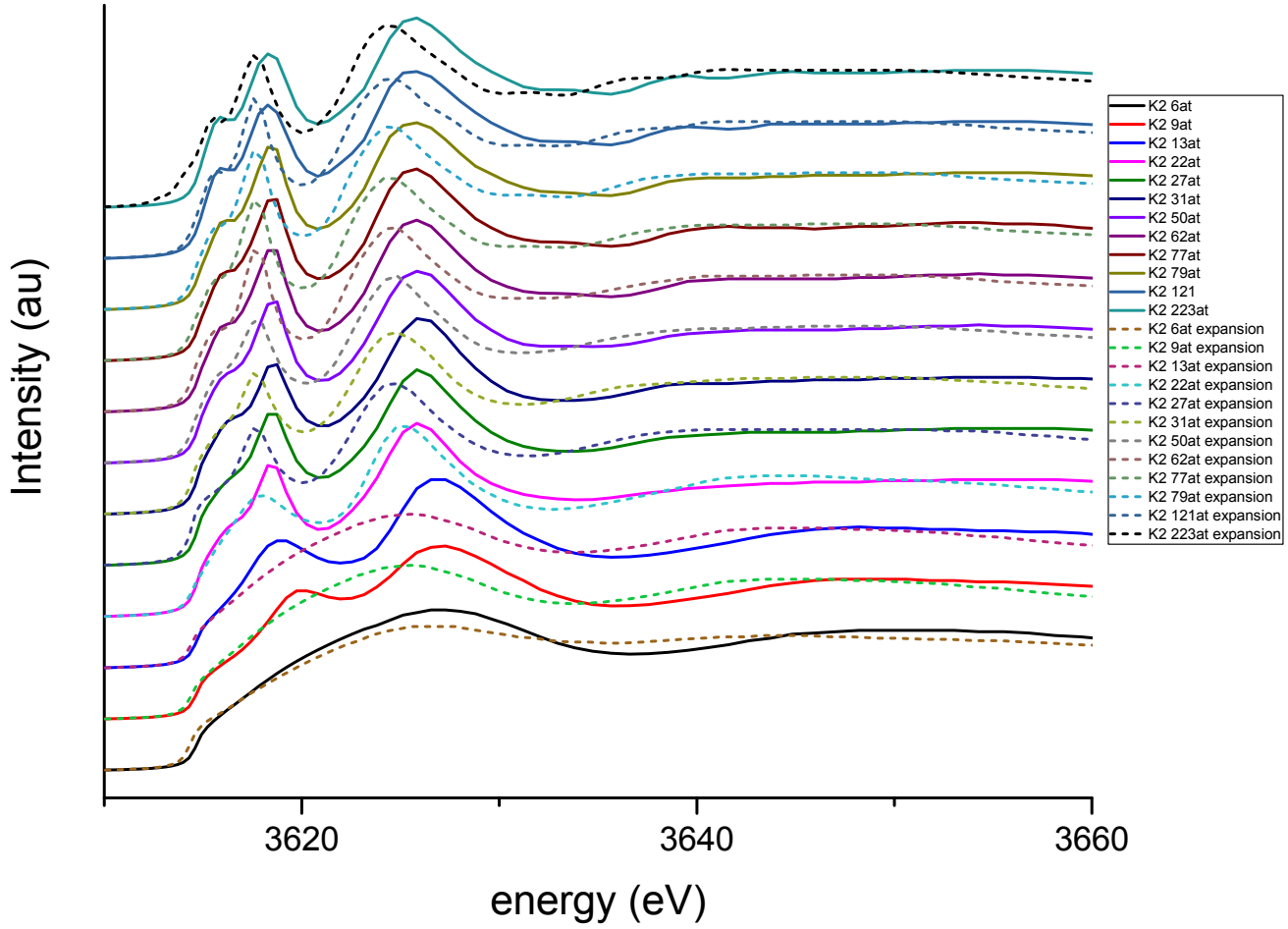


Figure 10. *K_2CO_3 K2 clusters compared with 5 percent expansion of bond lengths*

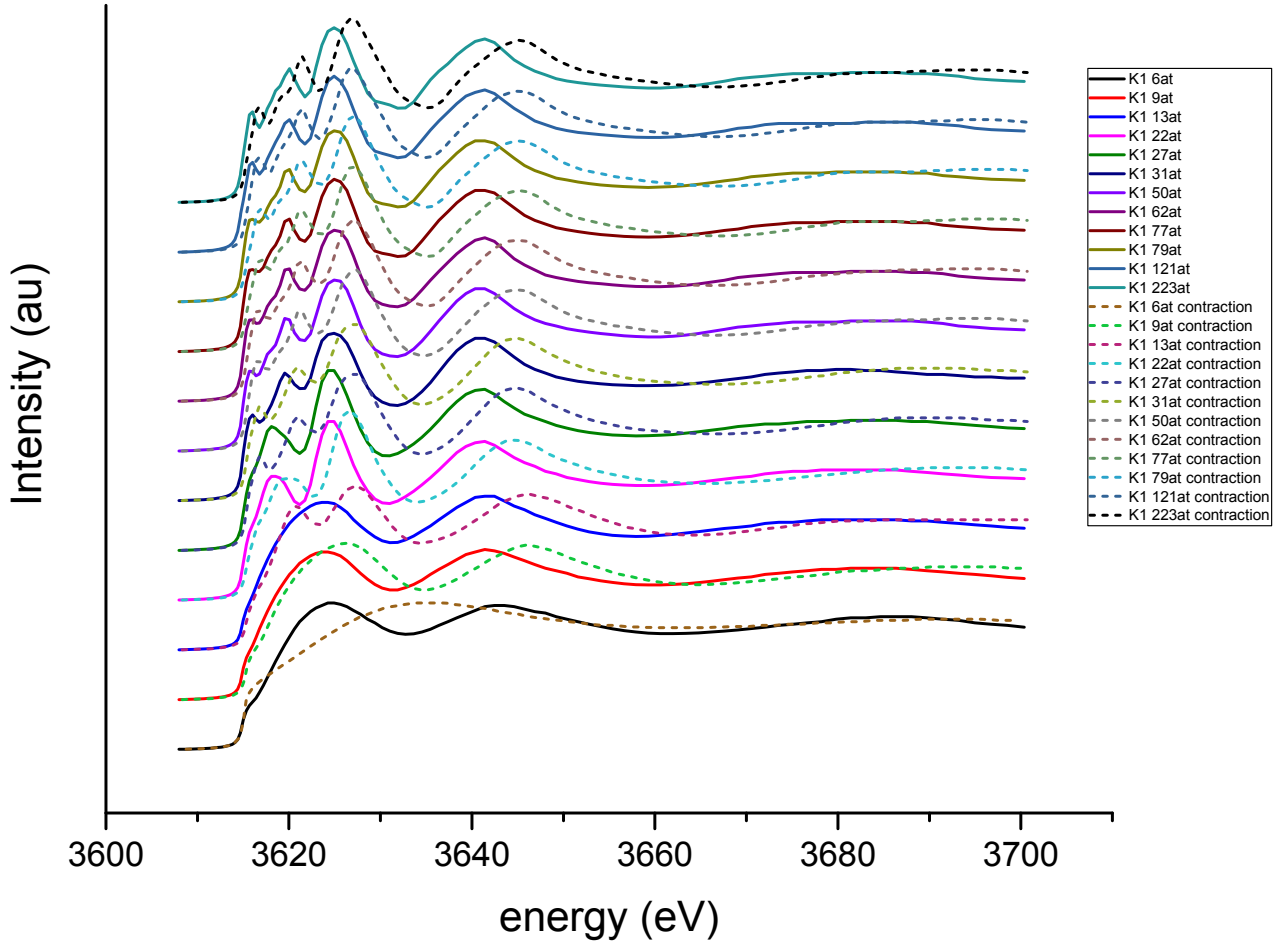


Figure 11. *K_2CO_3 K1 clusters compared with 5 percent contraction of bond lengths*

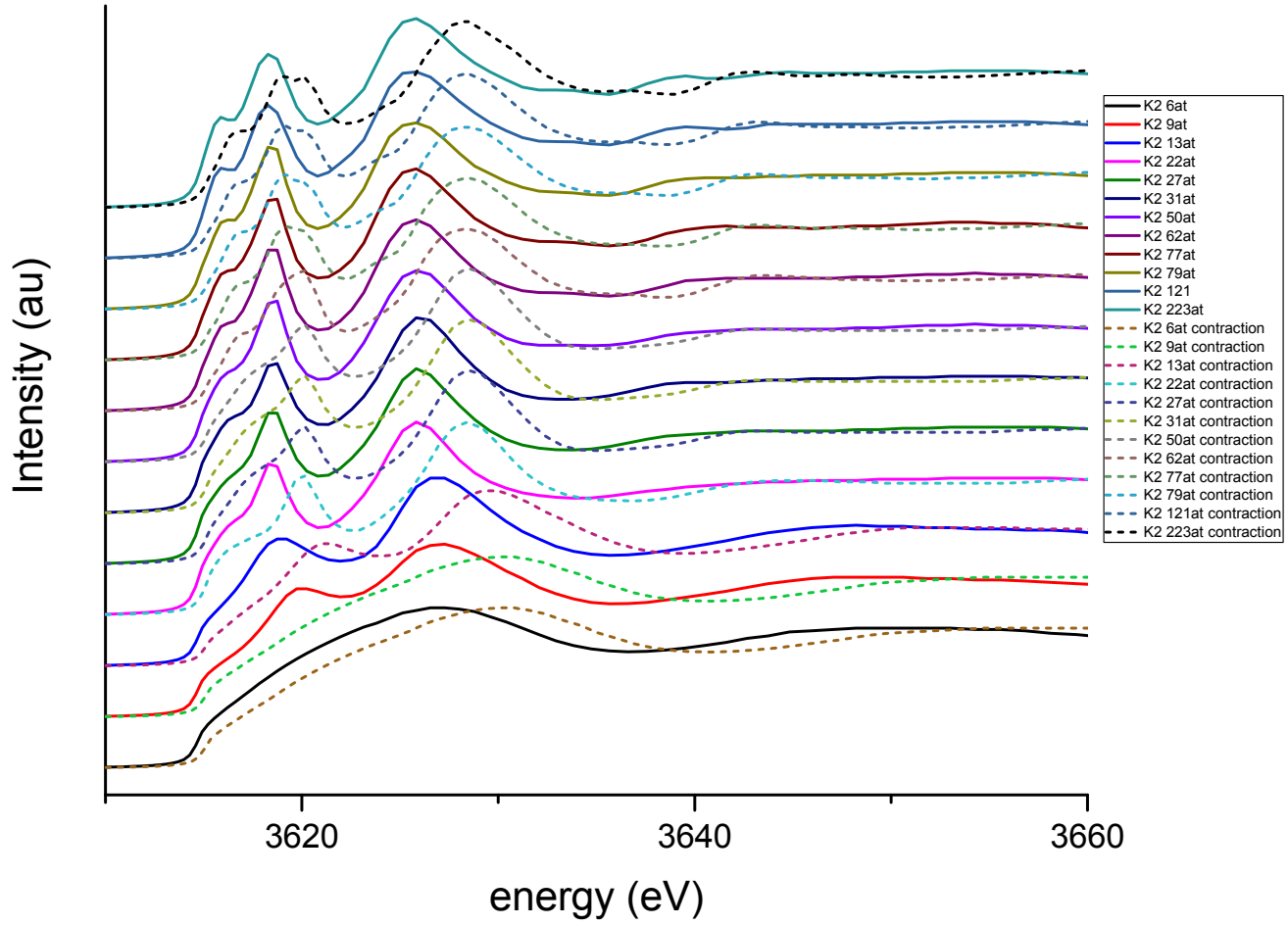


Figure 12. *K_2CO_3 K2 clusters compared with 5 percent contraction of bond lengths*

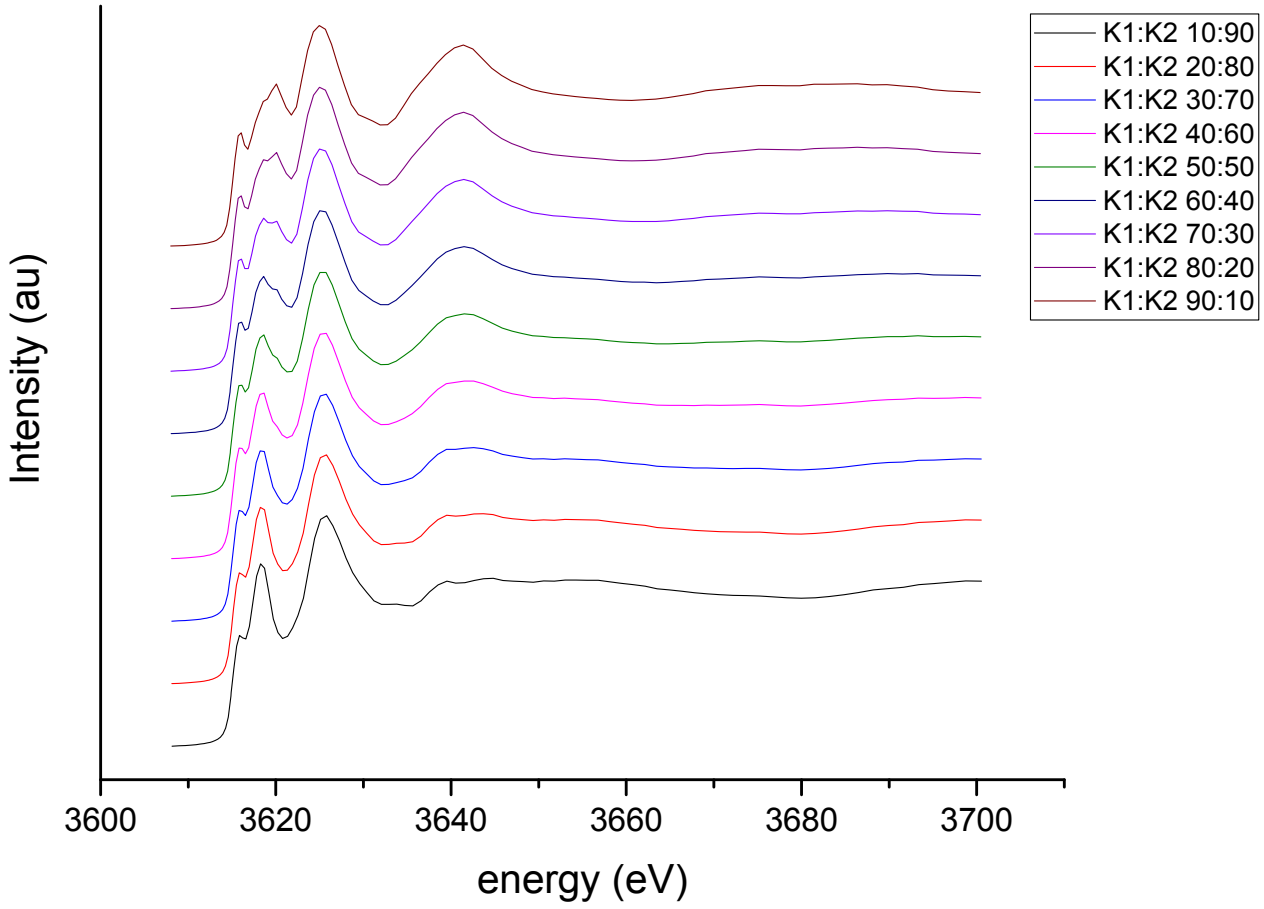


Figure 13. *Changing ratios for the contribution of K1 and K2 in K_2CO_3*

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.*