Electronic Supplementary Information

for

Anomalous Chemical Shifts in X-ray Photoelectron Spectra of Sulfur-Containing Compounds of Silver (I) and (II)

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1. Synthetic procedures

Ag_2O, AgO, Ag_2SO_4 and $AgSO_3CF_3$ were purchased from Sigma-Aldrich. $AgHSO_4$ was prepared by reacting Ag_2SO_4 and concentrated sulfuric acid (95-98%, Aldrich), crystallizing the product at 5°C and rinsing it with trifluoroacetic acid (≥99%, Aldrich).[14] $AgSO_4$ was obtained from AgF_2 (98%, Aldrich) and concentrated sulfuric acid (96-99%, Aldrich) according to the procedure described in [15]. $Ag_2S_2O_7$ was synthesized by heating $AgSO_4$ for 20 minutes at 150°C. $AgSO_3F$ was prepared in the reaction of AgF (99.9% trace metal basis, Aldrich) and HSO_3F (purified by triple distillation, Aldrich). Ag foil (99.995%) and Cu (99.99%) reference were obtained from SPECS.

2. Description of the XPS spectrometer and technical parameters used for measurements.

Overview

X-ray photoelectron spectra were measured using a custom-designed system made by SPECS (Fig. 2.1). The system consists of high vacuum chambers: a measurement chamber (where the pressure down to ca. 10^{-10} mbar is typically reached) and an antechamber (loadlock), connected to MBraun LABSTAR glovebox filled with Ar (monitored O_2 and H_2O levels, typically <0.5 ppm). The system allows characterisation of a sample by the means of XPS, UPS and Auger spectroscopy, as well as low-energy electron diffraction (LEED) and electron microscopy (SEM). The samples can be loaded and conditioned in the broad temperature range (ca. 90 - 773 K). The system is also equipped with an ion gun IQE 11 (Ar 99.999% was used as an ion source, beam energy up to 5 keV, beam current up to 10 mA) and a knife for the

surface cleaning and refreshing under high vacuum. The electron flood gun FG 15/40 was used for the charge compensation; this device allows operation at the electron energies up to 500 eV and currents up to 1 mA. The mass spectrometer LC-D DYCOR from Ametek Process Instruments was used for inspection of the atmosphere of the measurement chamber.

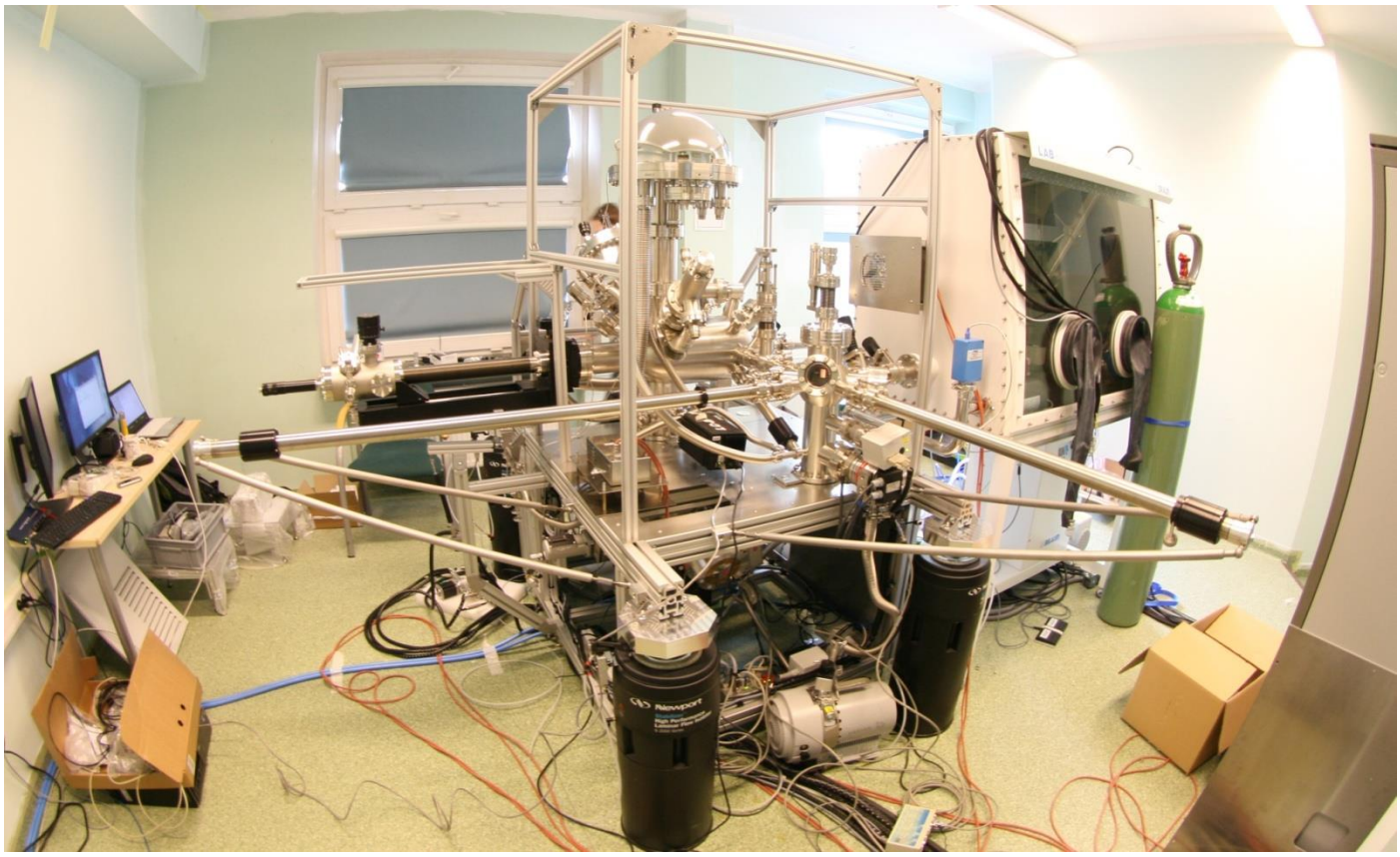

Fig. 2.1. The overview of the SPECS measurement system (XPS/UPS/LEED/SEM/Auger) connected to the MBraun glovebox.

XPS

The X-ray source XR50 M is equipped with a dual anode (Al and Ag) facilitating the measurements with the two photon energies. The spectra presented in this paper were recorded solely with Al Kα line (1486.74 eV, resolution 0.25 eV) at 32 mA emission current and 12.5 kV anode bias (400 W). A single crystal quartz mirror monochromator, the Phoibos 100 hemispherical analyser (100 mm mean radius) and a delayline electron detection system (DLD 3636) were used for the measurements. The analyser operated at 10 eV pass energy for the region scans of $AgSO_4$ and 20 eV for all other scans, with the entrance slit 7x20 mm and the open exit slit, 20x39 mm. The medium area lens mode was used for the measurements, which corresponds to the spectrum accumulated from the spot of ca. 2 mm radius.

3. Sample preparation.

The samples were loaded in a holder provided by SPECS via a glove box in argon atmosphere, except for Ag_2O, which was pressed into a pellet and loaded in air atmosphere directly into the load lock of the system, and Ag, which was provided inside the XPS system by the manufacturer. Ag and Cu foils were sputtered with Ar^+ ions at 10 mA and 1.5 keV for 20 minutes before spectra acquisition.

4. Spectra referencing procedure.

Electron flood gun was used to compensate for surface charging, although its use was unnecessary for Ag, Ag_2O, AgO, Ag_2SO_4 and $AgHSO_4$. The spectra were referenced to C 1s line of inadvertent hydrocarbon contamination (284.6 eV) in the case of Ag, Ag_2O, AgO, Ag_2SO_4 and $AgHSO_4$; F 1s line of CF_3 group in triflate anion (688.2 eV)[1] in the case of $AgSO_3CF_3$; and Ag $3d_{5/2}$ line of Ag_2SO_4 (368.0 eV) in the case of $AgSO_3F$, $AgSO_4$ and $Ag_2S_2O_7$.

5. Quantitative analysis of the elemental contents.

The composition of analysed surfaces was determined by integrating selected bands and dividing the results by their respective relative sensitivity factors (RSF) which are normalized to the C 1s band. The RSFs were Ag 3d – 18; O 1s – 2.93, S 2p – 1.68, C 1s – 1, F 1s – 4.43.

6. XPS spectra (not calibrated).

6.1. Metallic silver – Ag

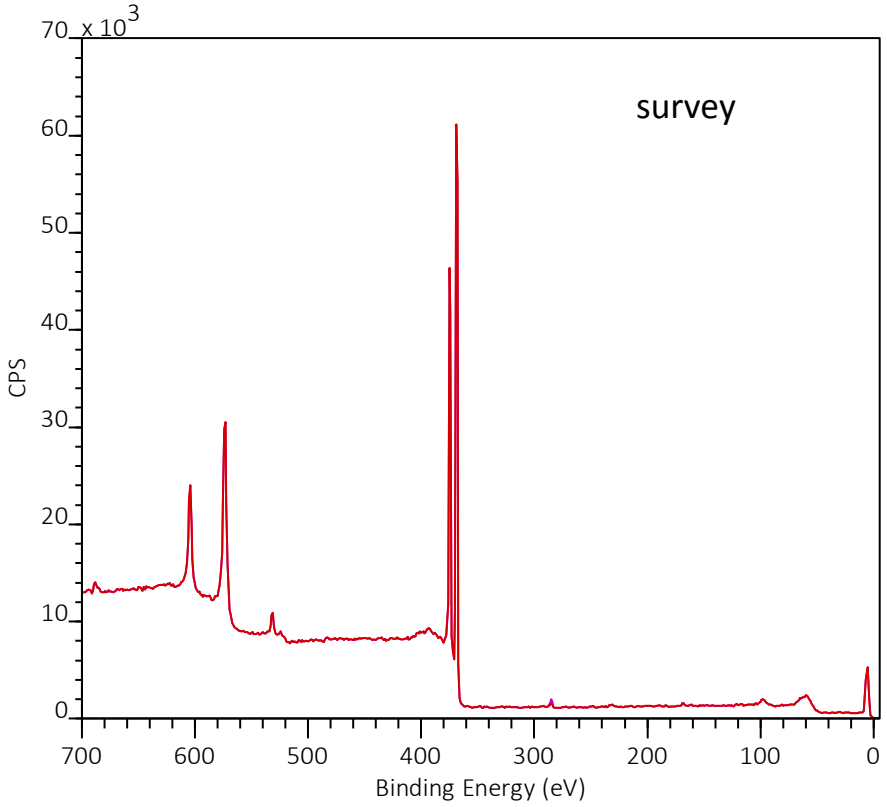

Fig. 6.1.1. Survey spectrum.

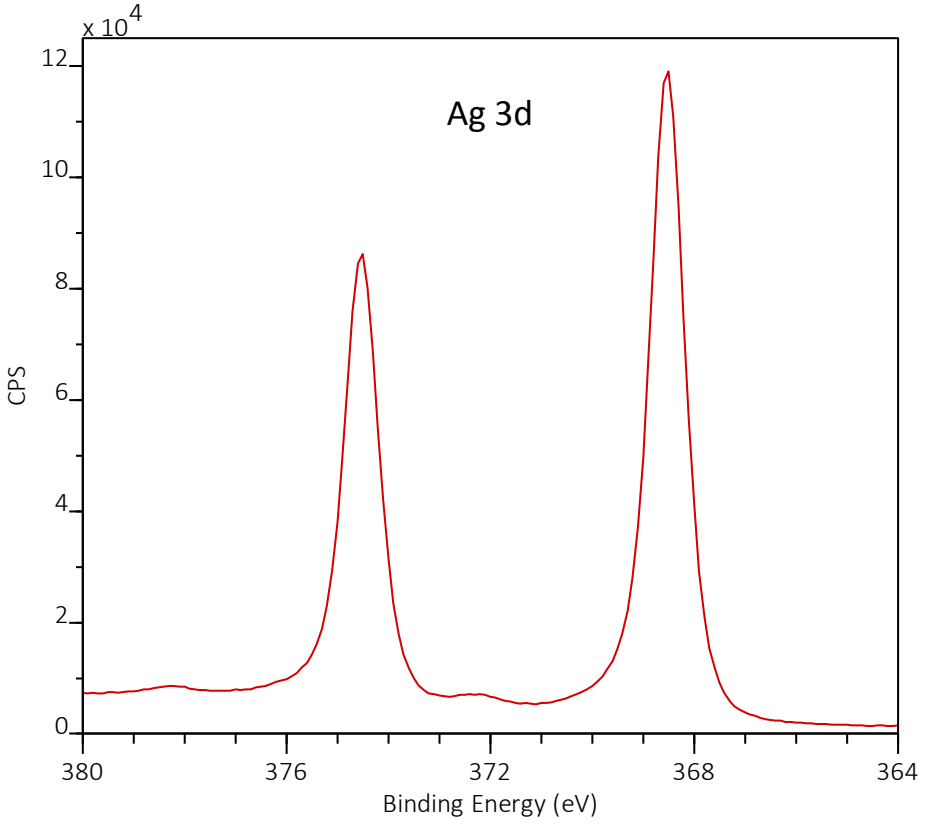

Fig. 6.1.2. Ag 3d region.

6.2. Silver (I) oxide – Ag_2O

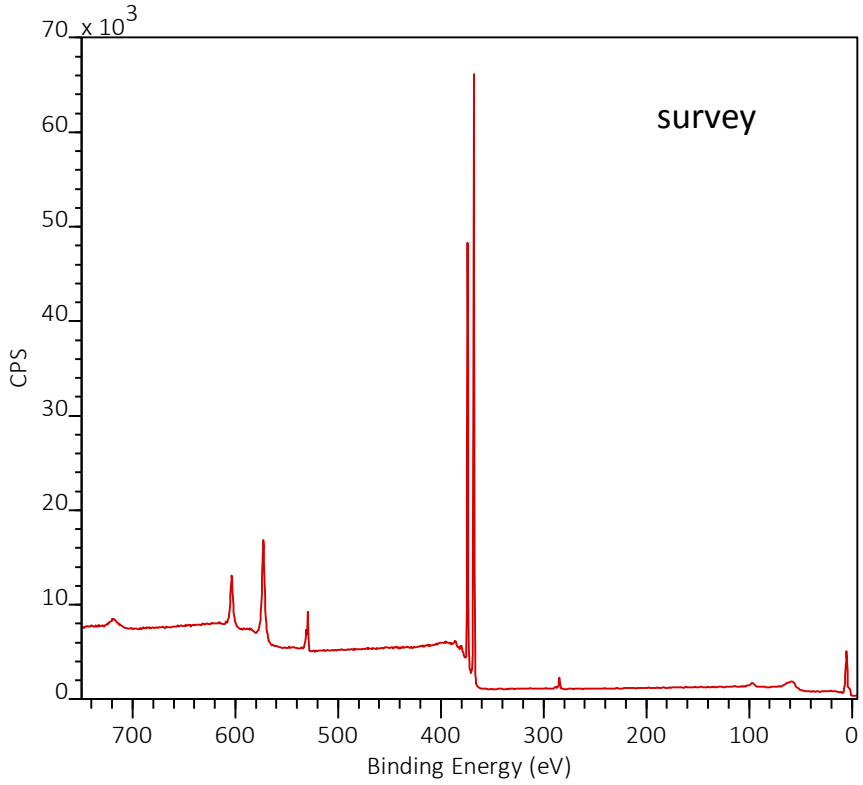

Fig. 6.2.1. Survey spectrum. Composition: Ag 54.0%, O 23.5%, C 22.5%.

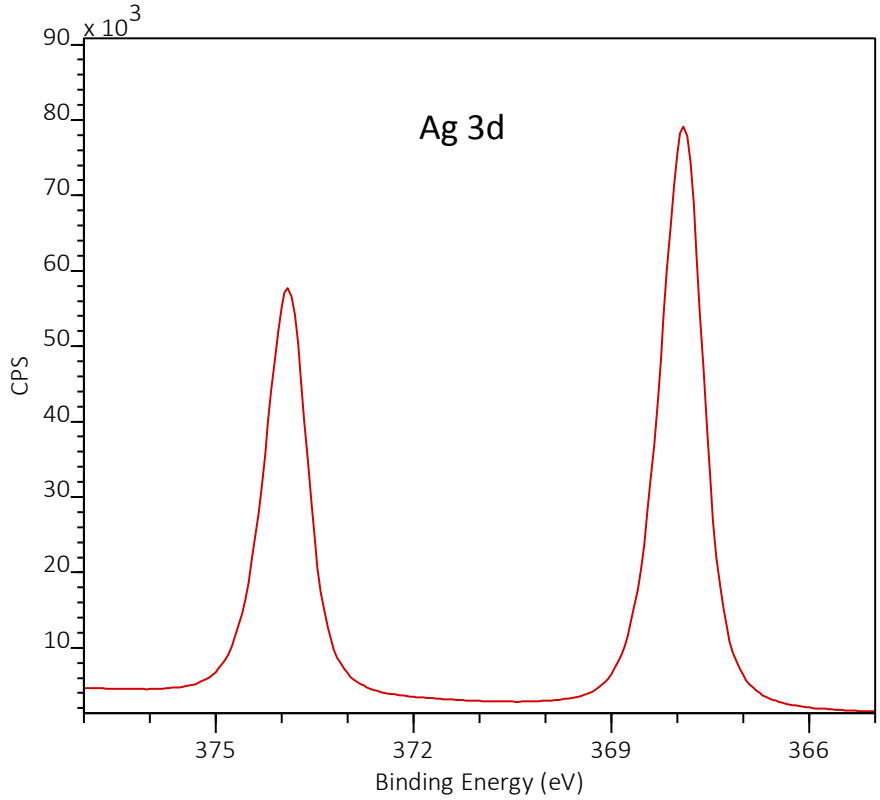

Fig. 6.2.2. Ag 3d region.

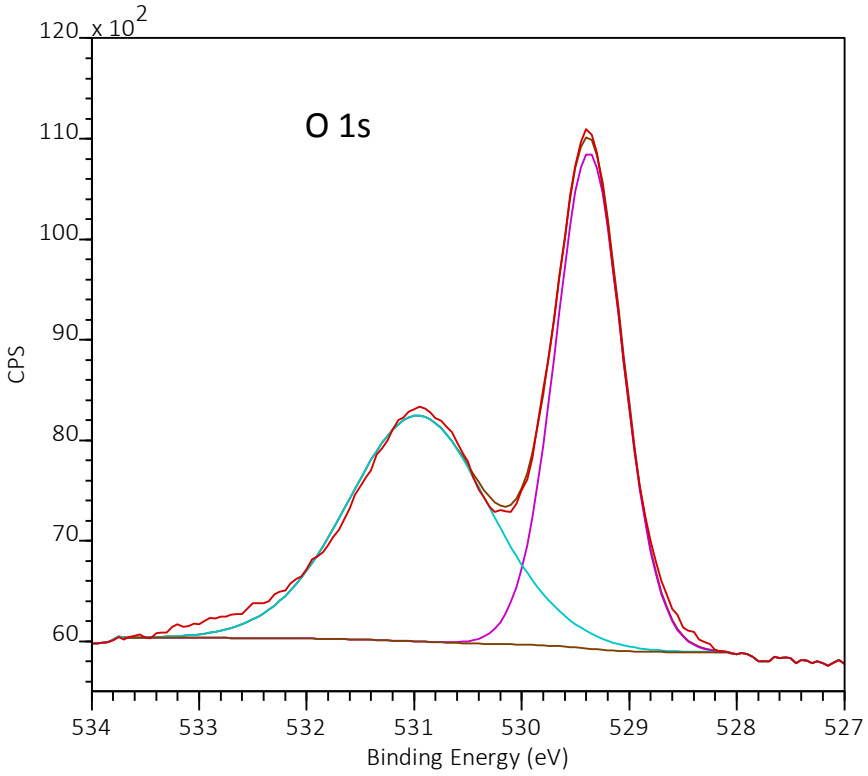

Fig. 6.2.3. O 1s region. 529.4 eV –Ag_2O, 531.0 eV – Ag_2CO_3/$AgHCO_3$.

6.3. Silver (I,III) oxide – AgO

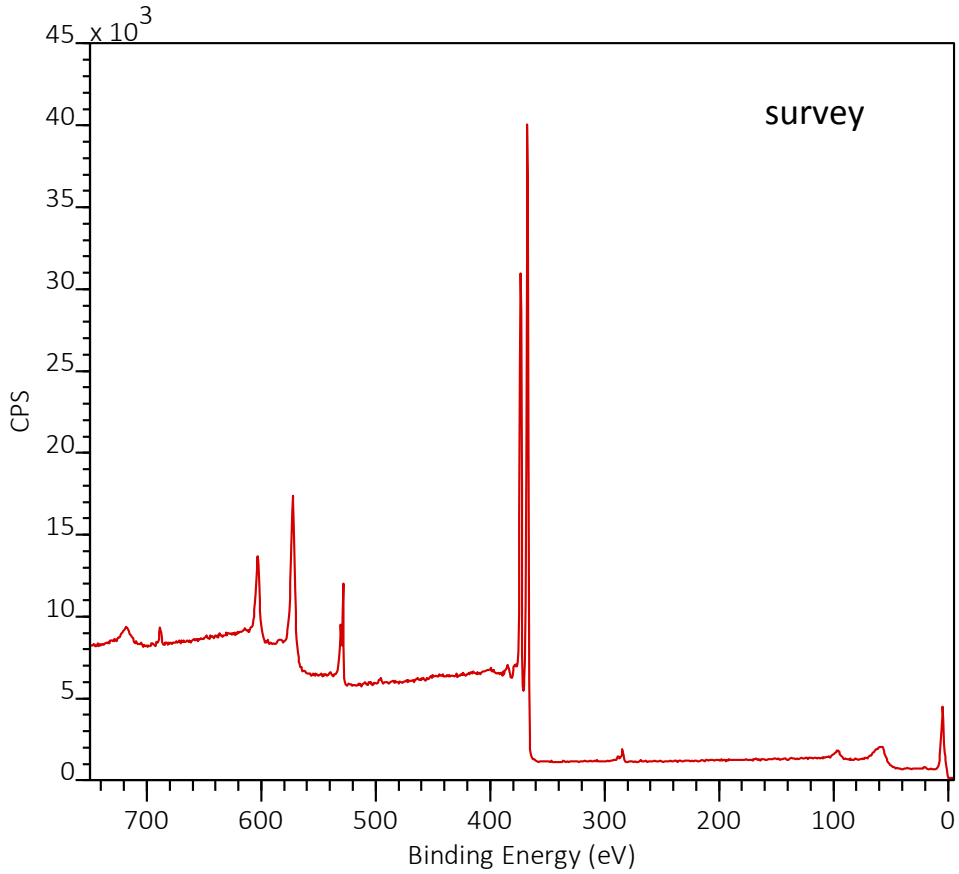

Fig. 6.3.1. Survey spectrum. Composition: Ag 52.8%, O 32.8%, C 14.4%.

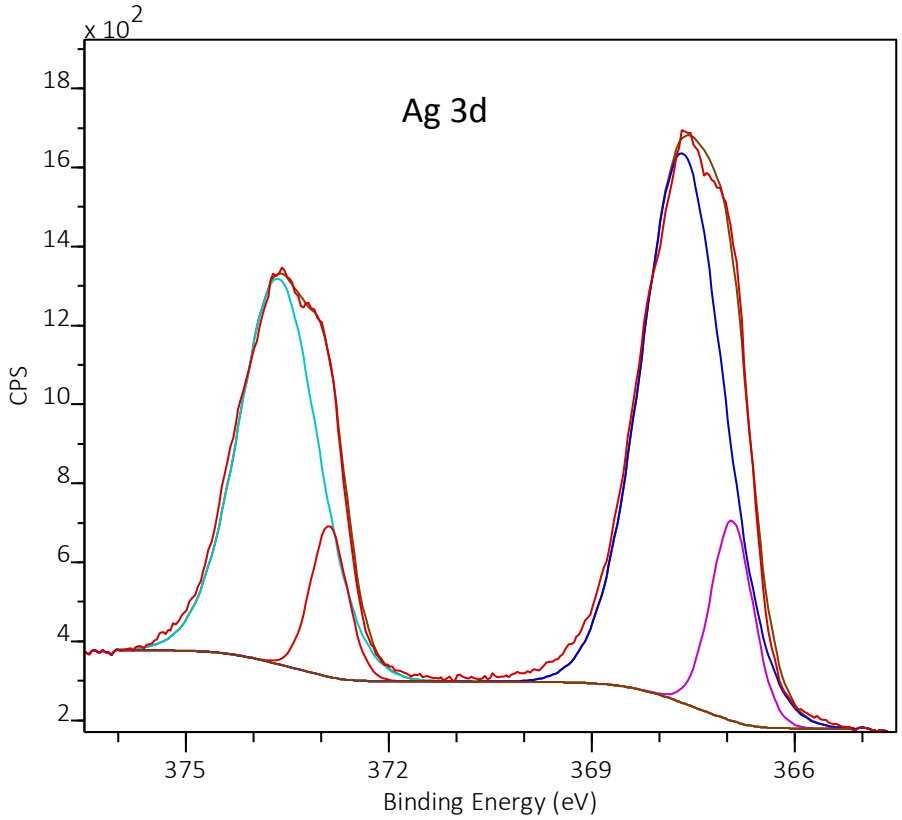

Fig. 6.3.2. Ag 3d region. 367.7 eV, 373.7 eV – Ag^{I}. 366.9 eV, 372.9 eV – Ag^{III}. Ag^{I}/Ag^{III} = 5.5.

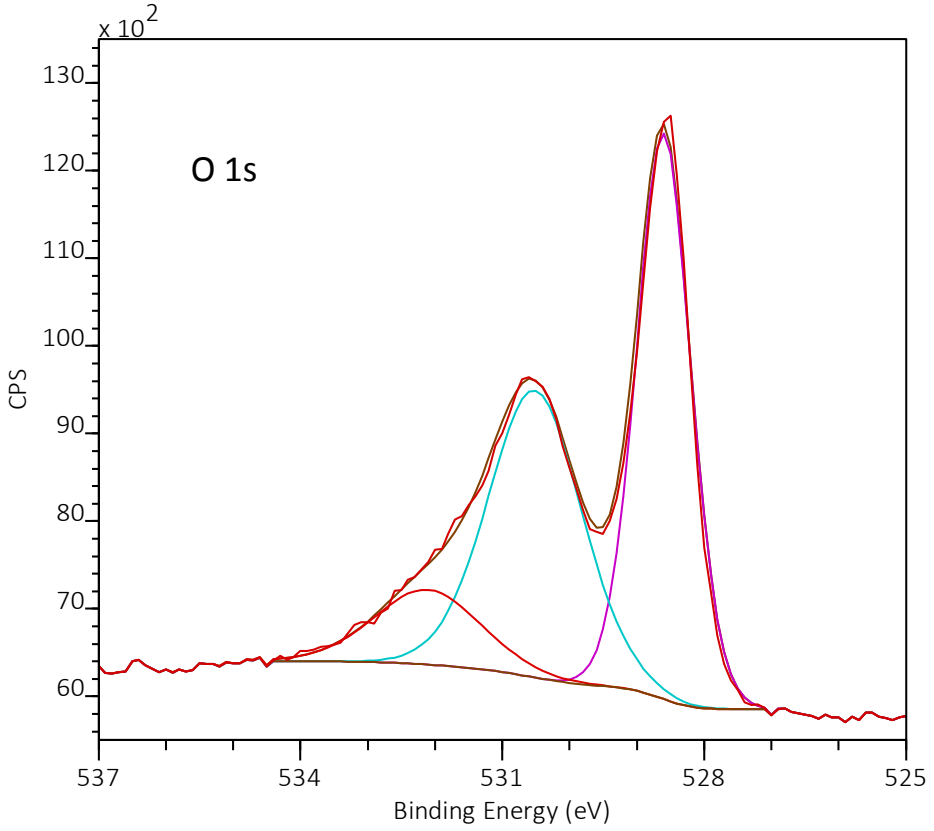

Fig. 6.3.3. O 1s region. 528.6 –AgO, 530.5 eV – Ag_2CO_3, 532.1 eV – subsurface O.

6.4. Silver (I) sulphate – Ag_2SO_4

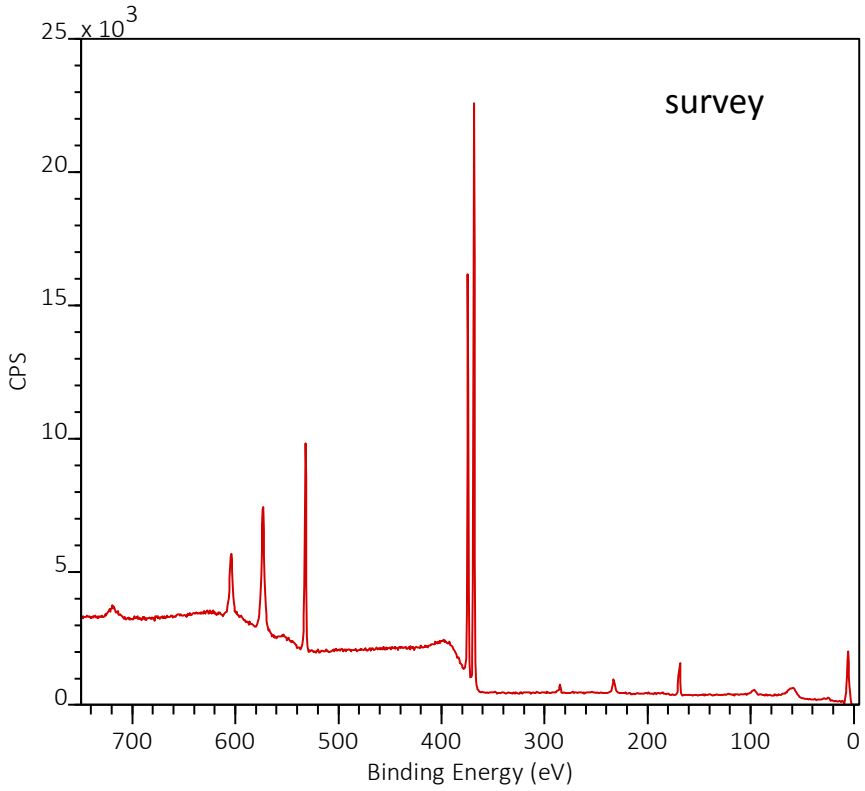

Fig. 6.4.1. Survey spectrum. Composition: Ag 30.5%, S 16.8%, O 46.2%, C 6.5%.

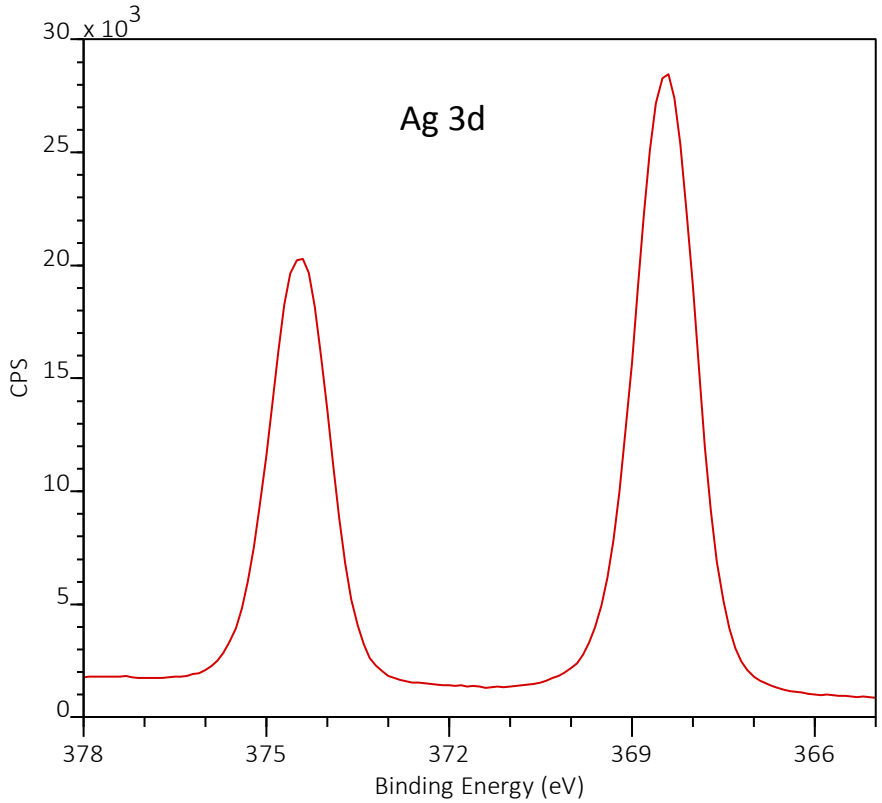

Fig. 6.4.2. Ag 3d region.

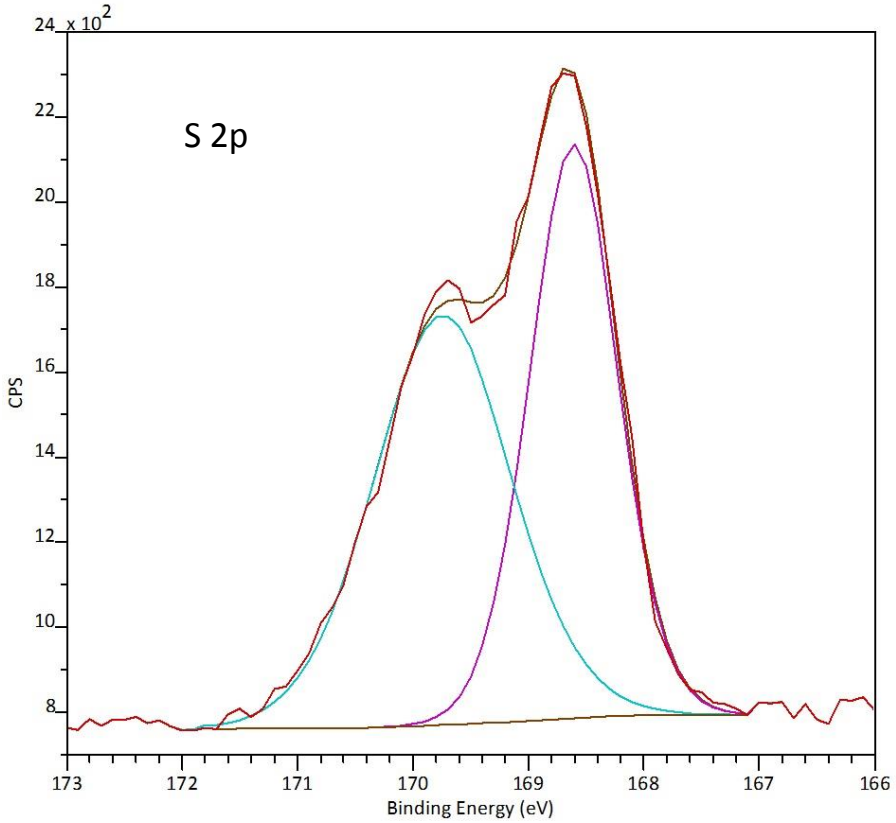

Fig. 6.4.3. S 2p region.

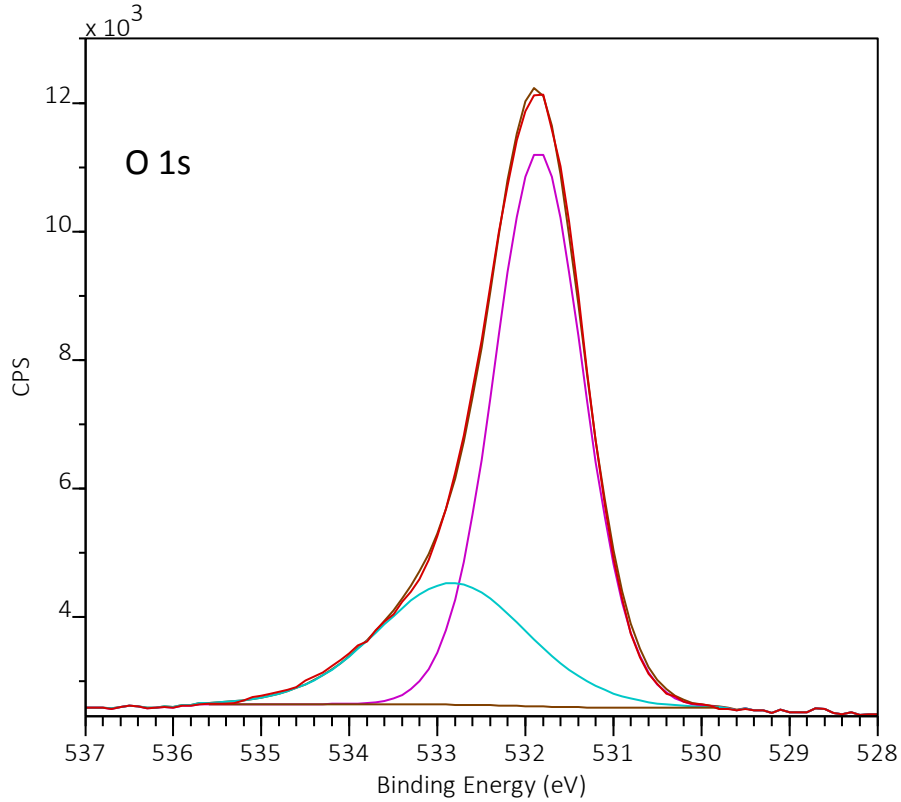

Fig. 6.4.4. O 1s region.

6.5. Silver (I) hydrogen sulphate – $AgHSO_4$

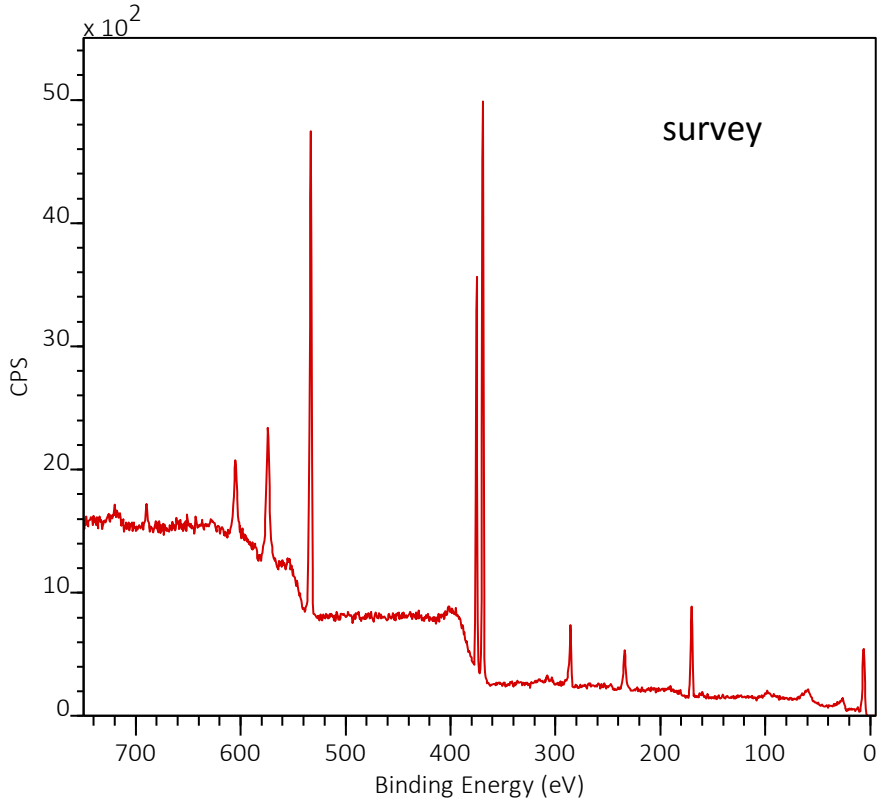

Fig. 6.5.1. Survey spectrum. Composition: Ag 12.5%, S 17.5%, O 48.2%, C 21.8%.

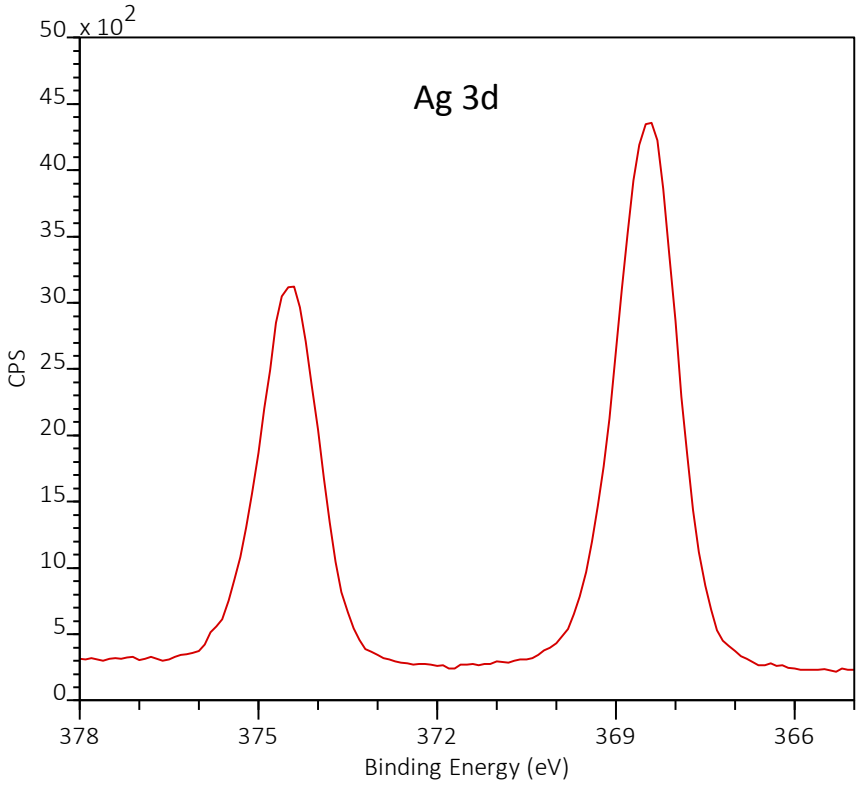

Fig. 6.5.2. Ag 3d region.

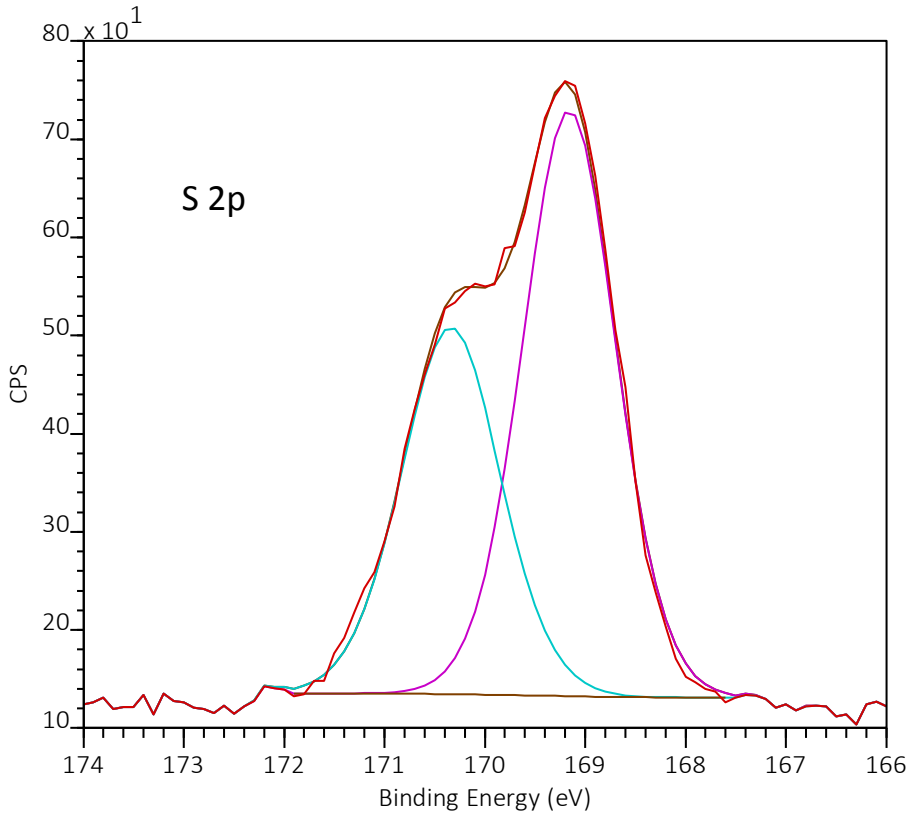

Fig. 6.5.3. S 2p region.

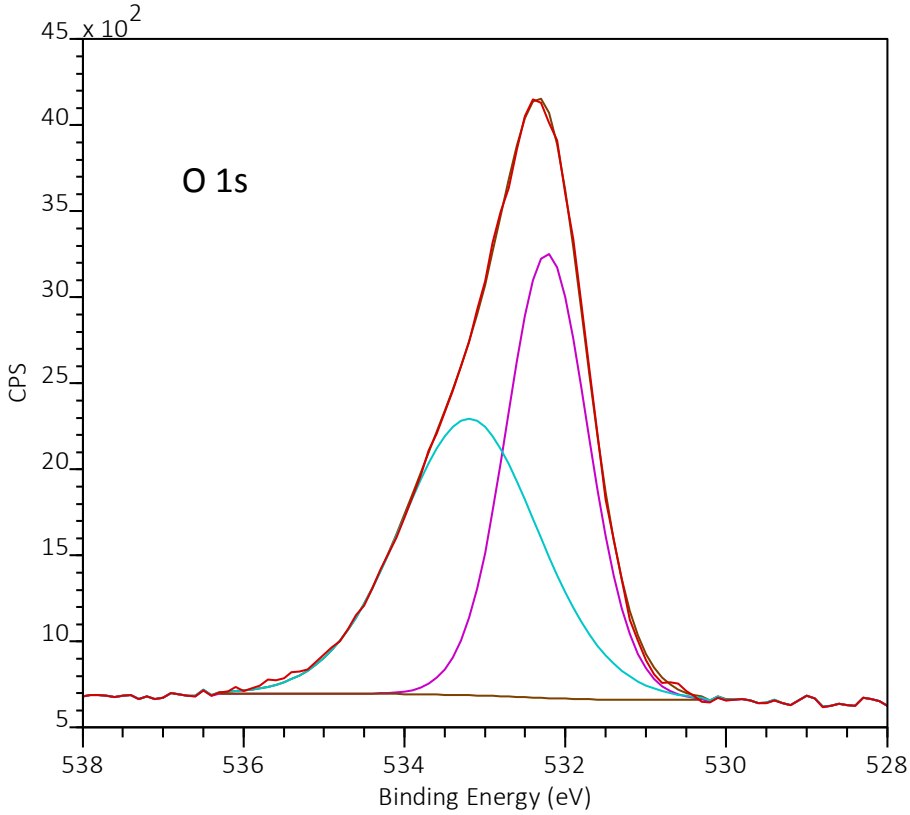

Fig. 6.5.4. O 1s region.

6.6. Silver (I) fluorosulphate – $AgSO_3F$

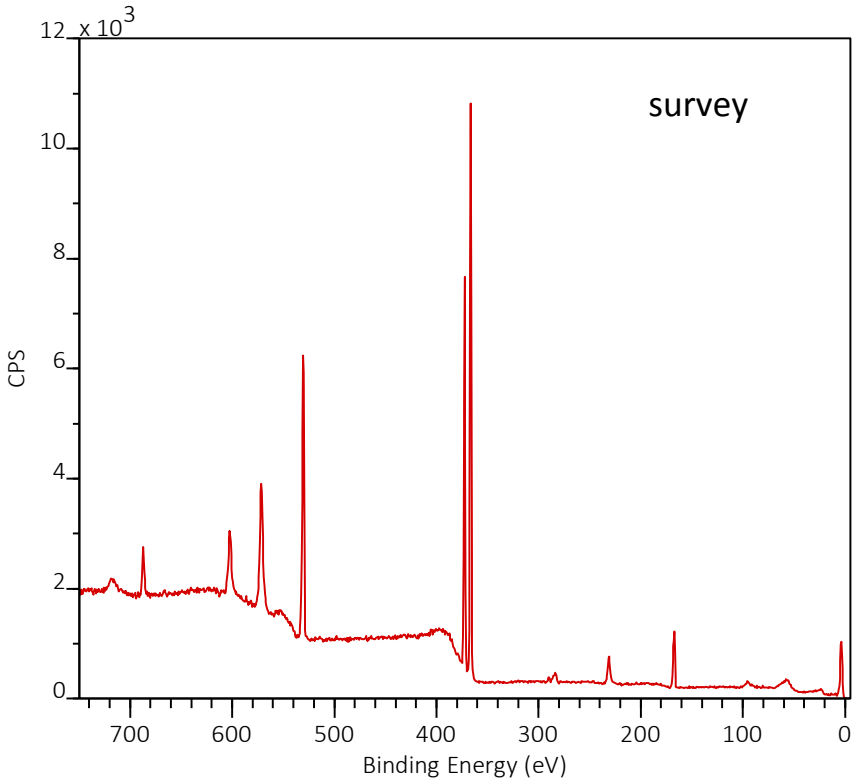

Fig. 6.6.1. Survey spectrum. Composition: Ag 19.5%, S 18.6%, O 46.6%, F 5.0%, C 10.3%.

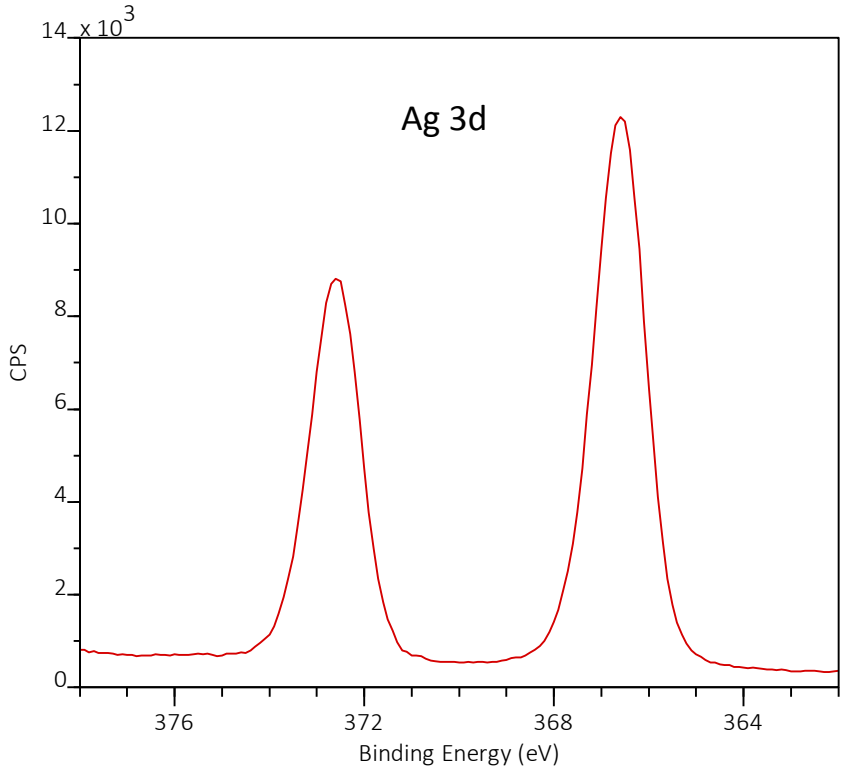

Fig. 6.6.2. Ag 3d region.

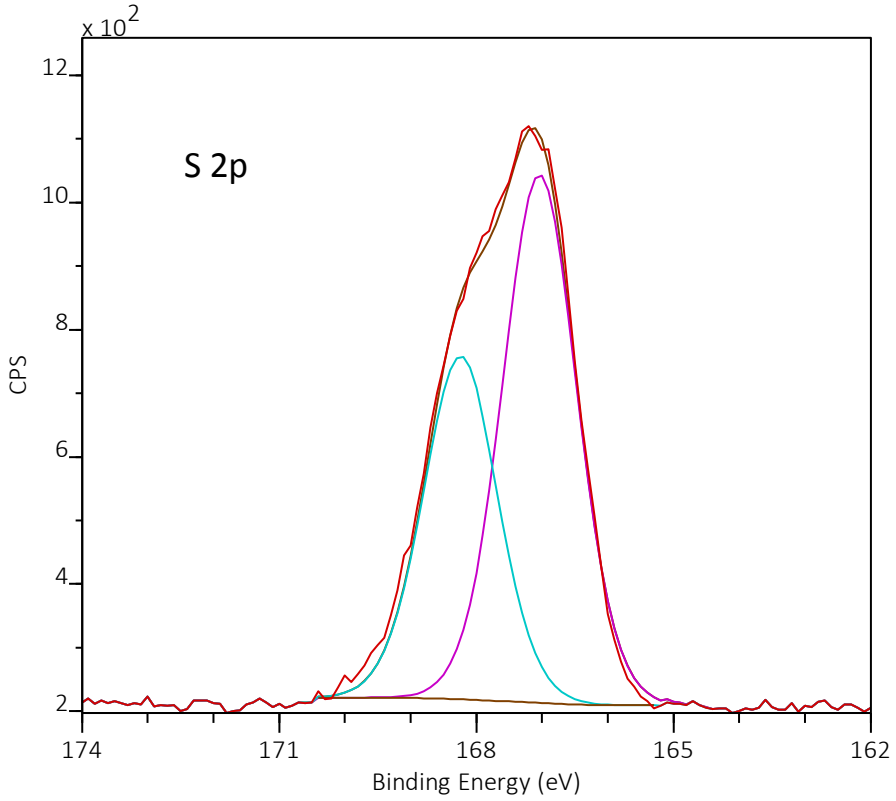

Fig. 6.6.3. S 2p region.

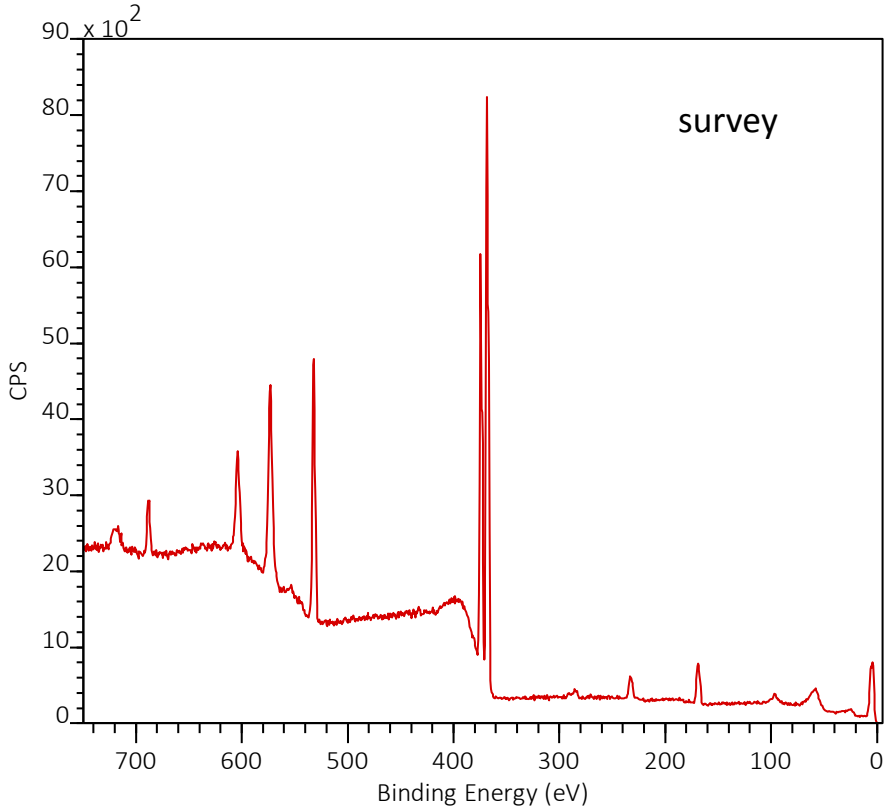

Fig. 6.6.4. Survey spectrum after 3 h of irradiation in UHV. Composition: Ag 26.0%, S 17.2%, O 42.3%, F 5.7%, C 8.8%.

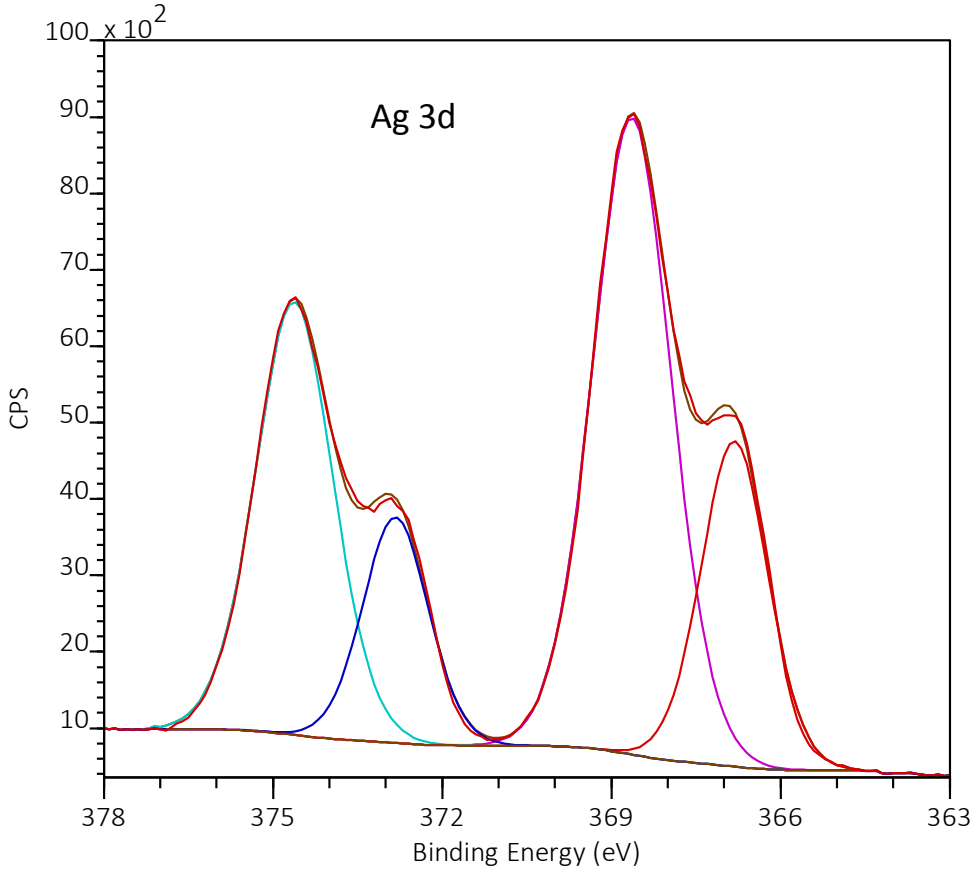

Fig. 6.6.5. Higher BE component – Ag_2SO_4, lower BE component – $AgSO_3F$.

6.7. Silver (I) triflate - $AgSO_3CF_3$

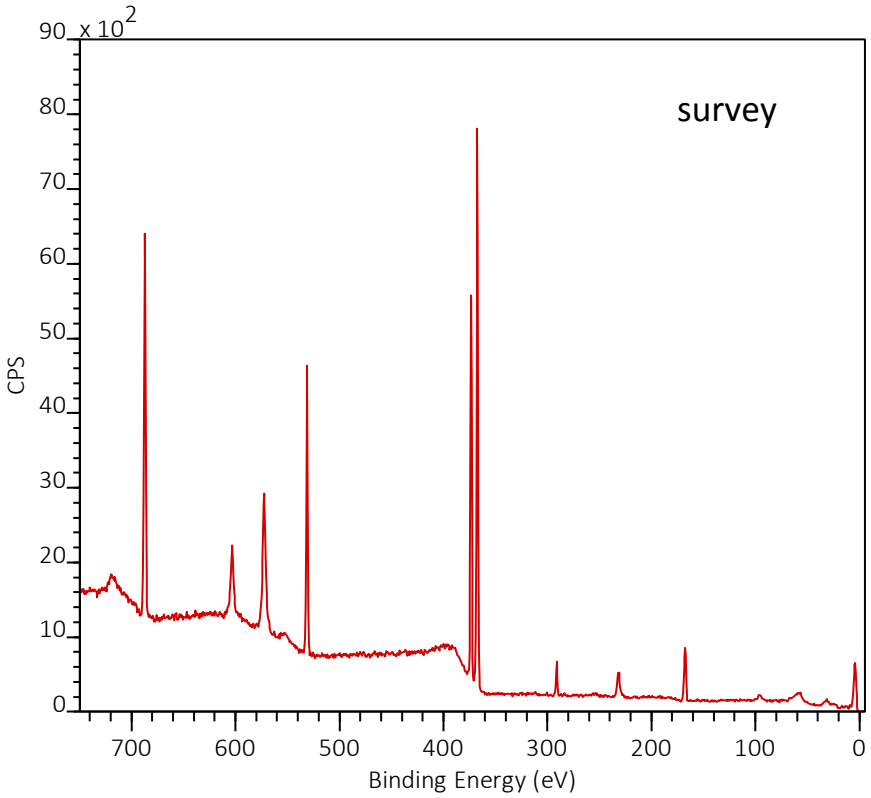

Fig. 6.7.1. Survey spectrum. Composition: Ag 16.0%, S 14.8%, O 29.1%, C 10.9%, F 29.2%.

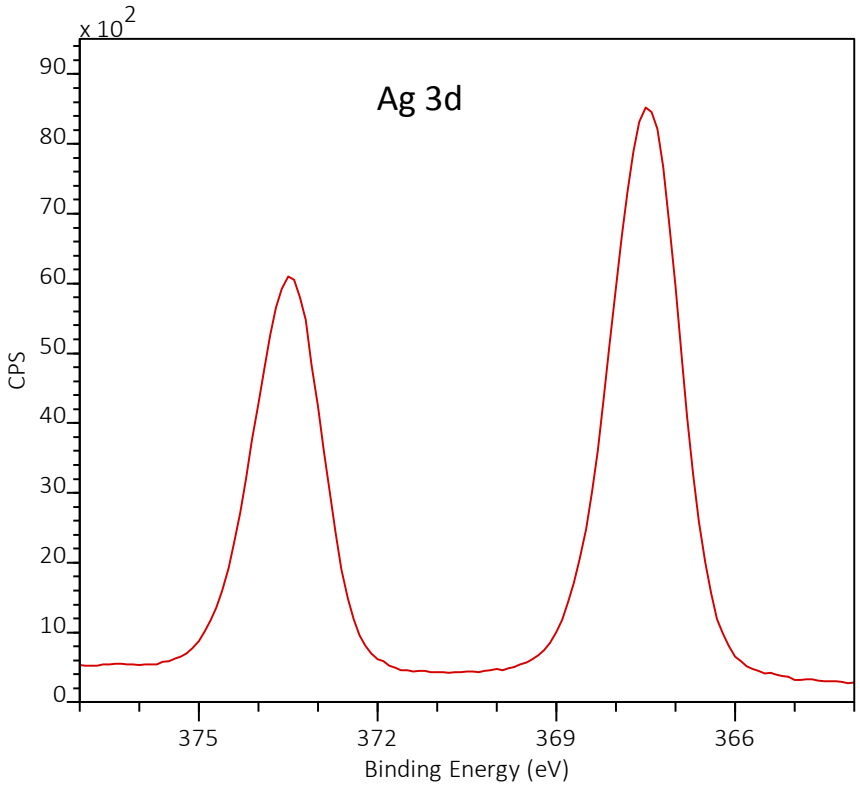

Fig. 6.7.2. Ag 3d region.

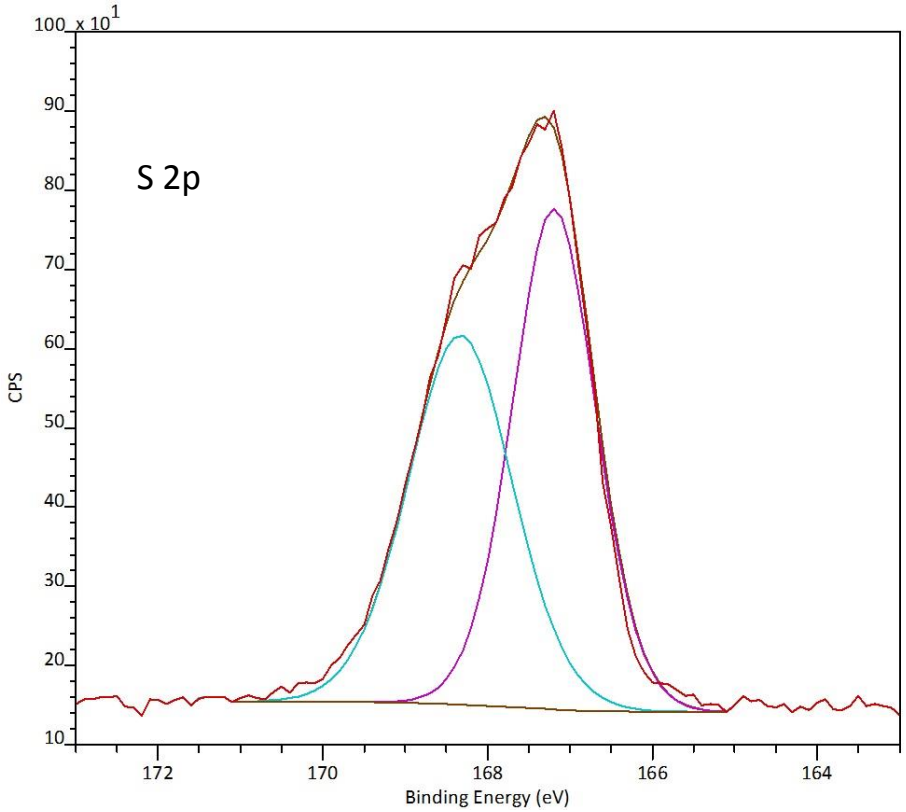

Fig. 6.7.3. S 2p region.

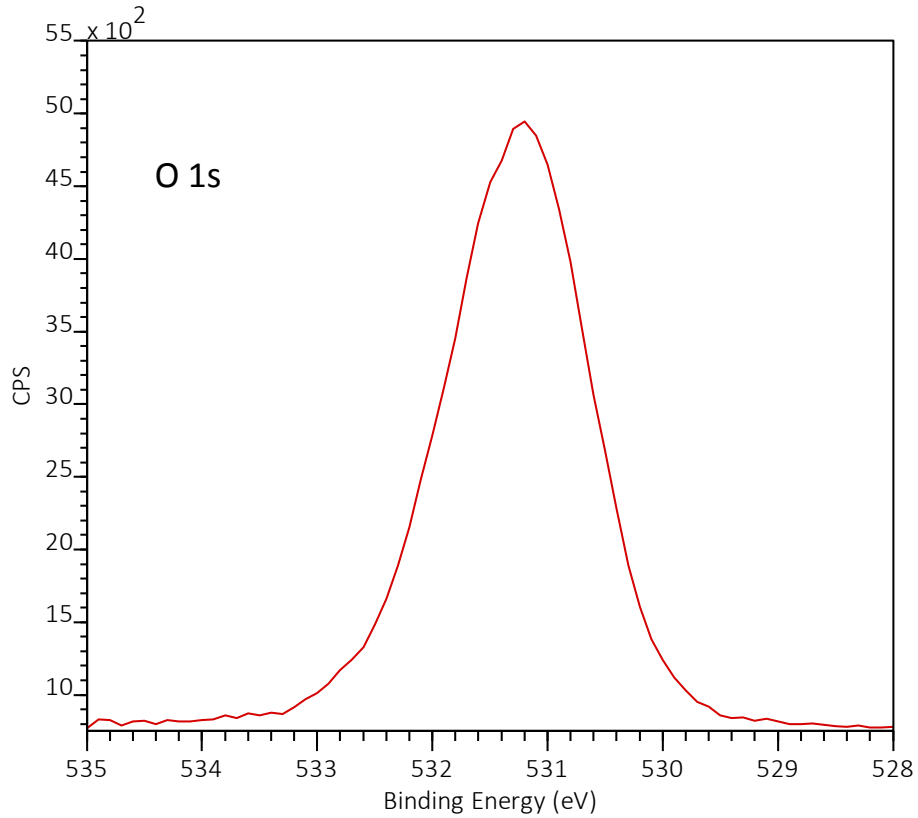

Fig. 6.7.4. O 1s region.

6.8. Silver (II) sulphate – $AgSO_4$

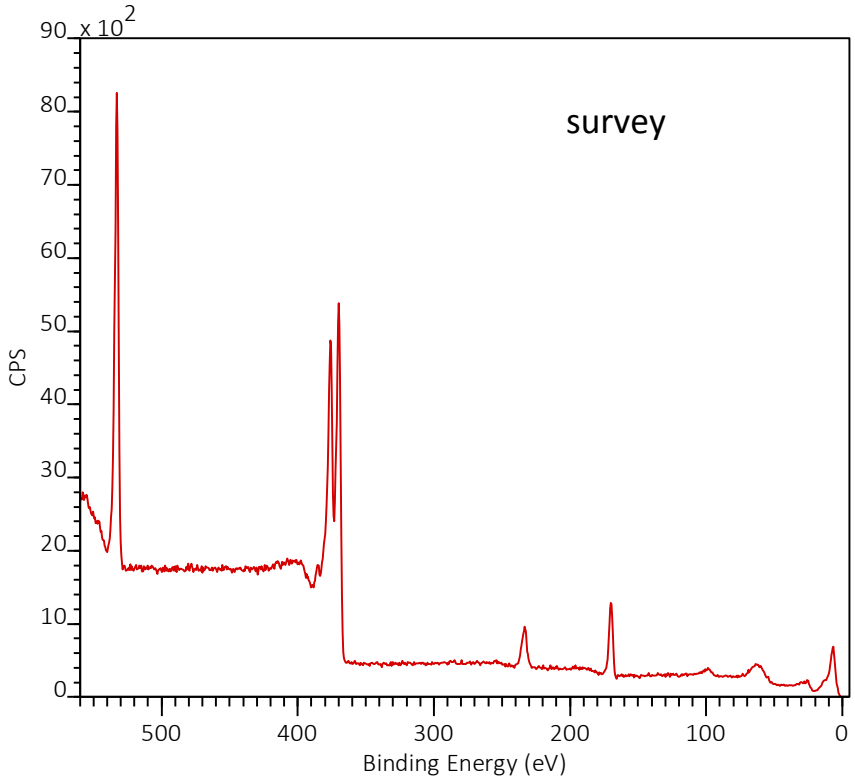

Fig. 6.8.1. Survey spectrum. Composition before heating: Ag 18.2%, S 20.9%, O 60.9%.

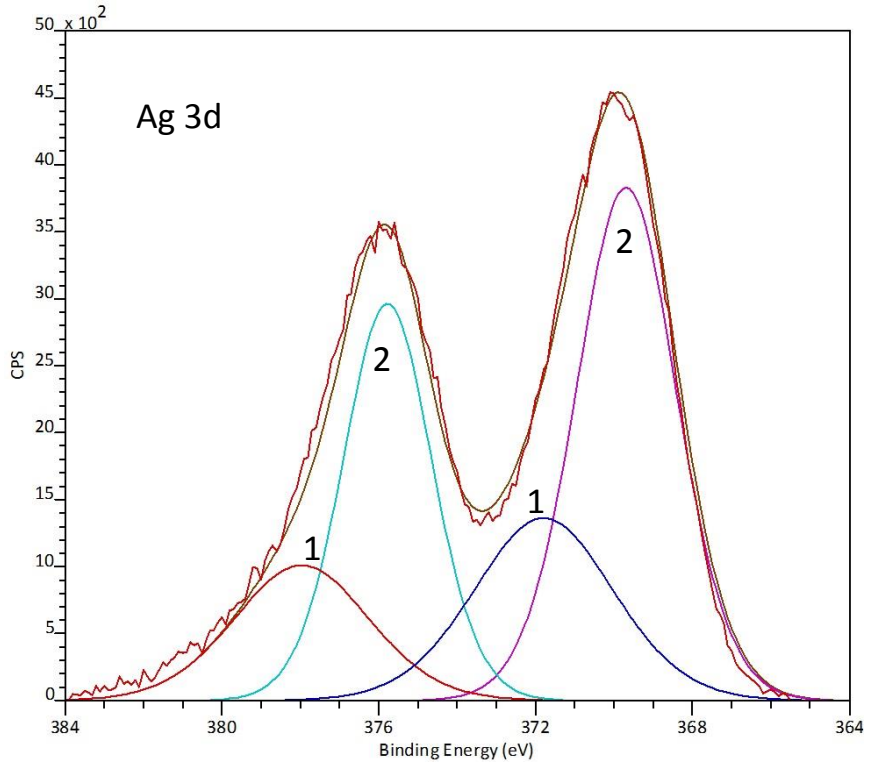

Fig. 6.8.2. Ag 3d region before heating.

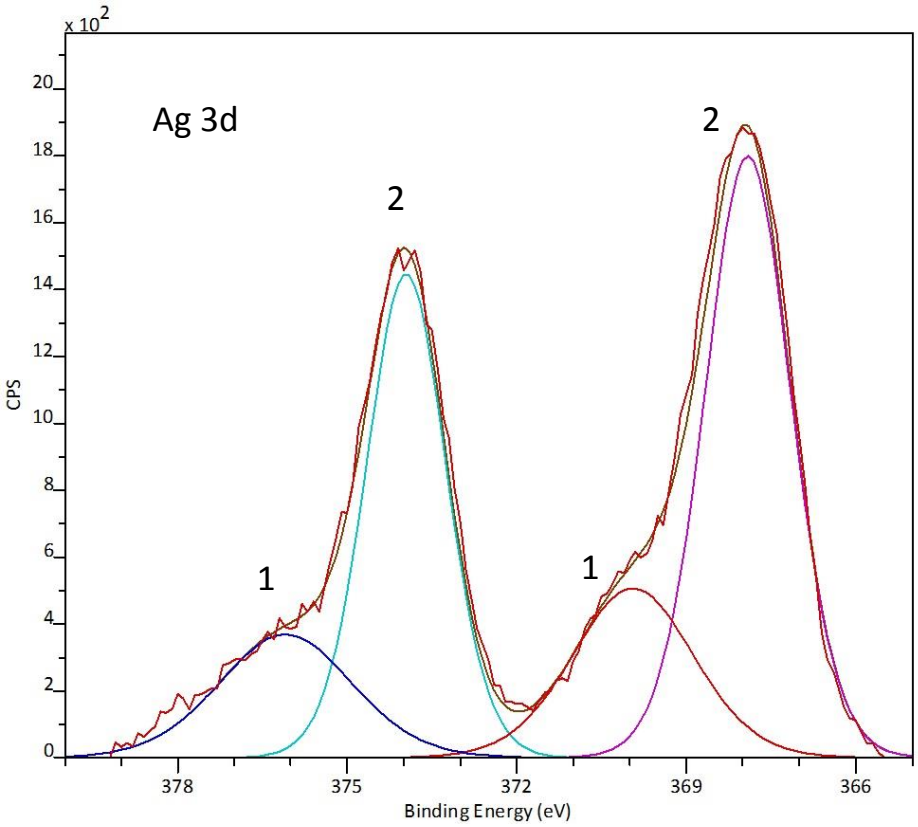

Fig. 6.8.3. Ag 3d region after heating to 35°C.

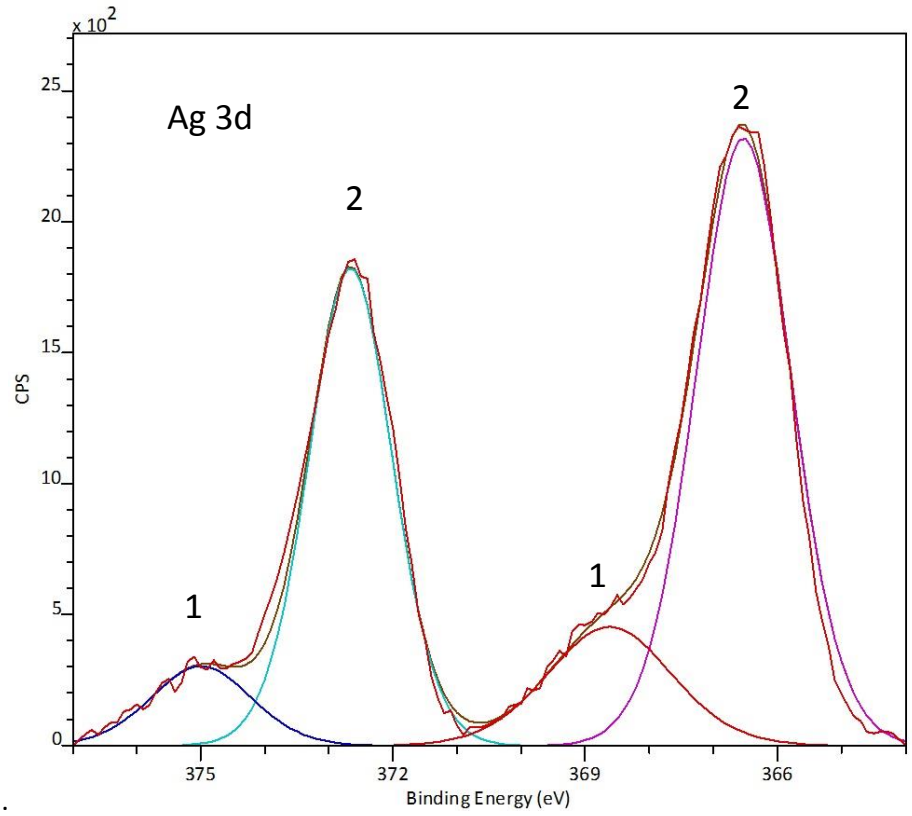

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Fig. 6.8.4. Ag 3d region after heating to 45°C

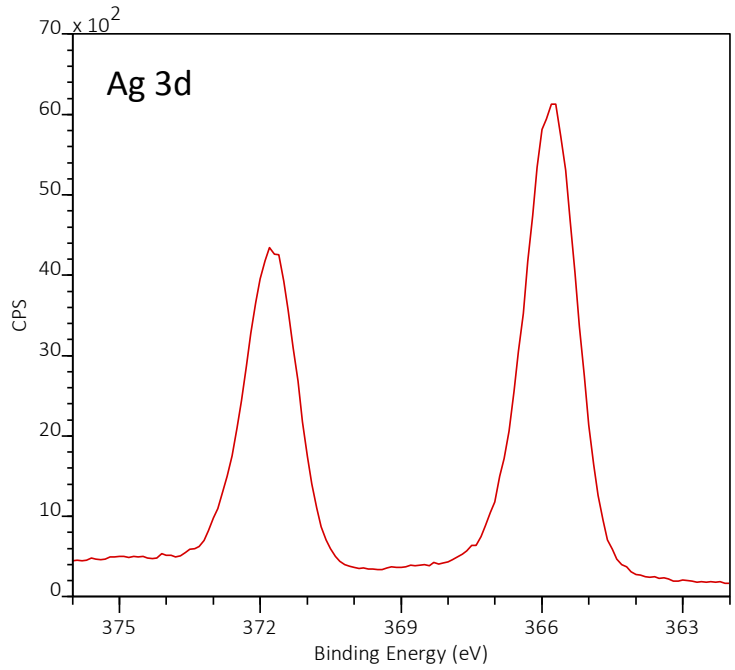


Fig. 6.8.5. Ag 3d region after heating to 50°C.

	Ag $3d_{3/2}$		Ag $3d_{5/2}$		Component 2 : Component 1
	1	**2**	**1**	**2**	
Initial, 25 °C	377.9	375.8	372.1	369.8	2.2
35°C	376.3	373.9	370.0	367.9	3.4
45°C	374.8	372.7	368.7	366.5	4.7
50°C	-	371.8	-	365.8	-

Table 6.8.1. Evolution of Ag 3d bands in time during the heating process.

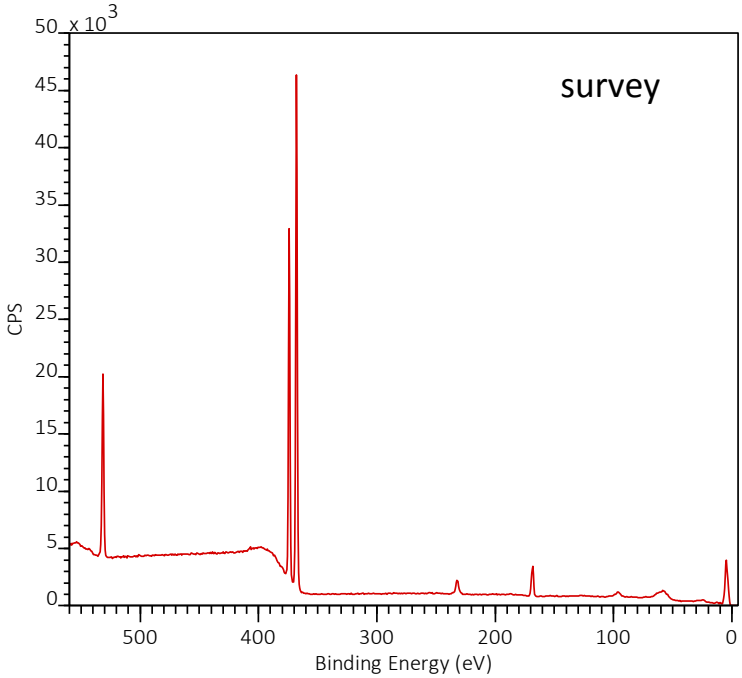


Fig. 6.8.6. Survey spectrum after heating to 50°C. Composition: Ag 34.0%, S 19.6%, O 46.4%.

6.9. Silver (I) disulphate – $Ag_2S_2O_7$

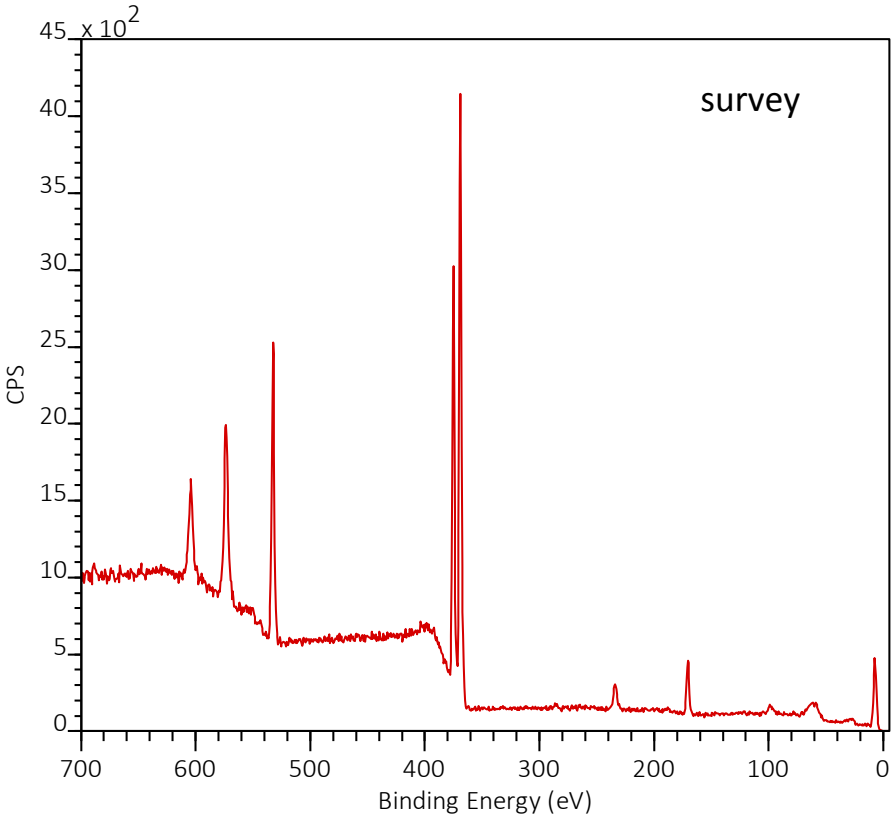


Fig. 6.9.1. Survey spectrum. Composition: Ag 26.4%, S 20.9%, O 52.7%

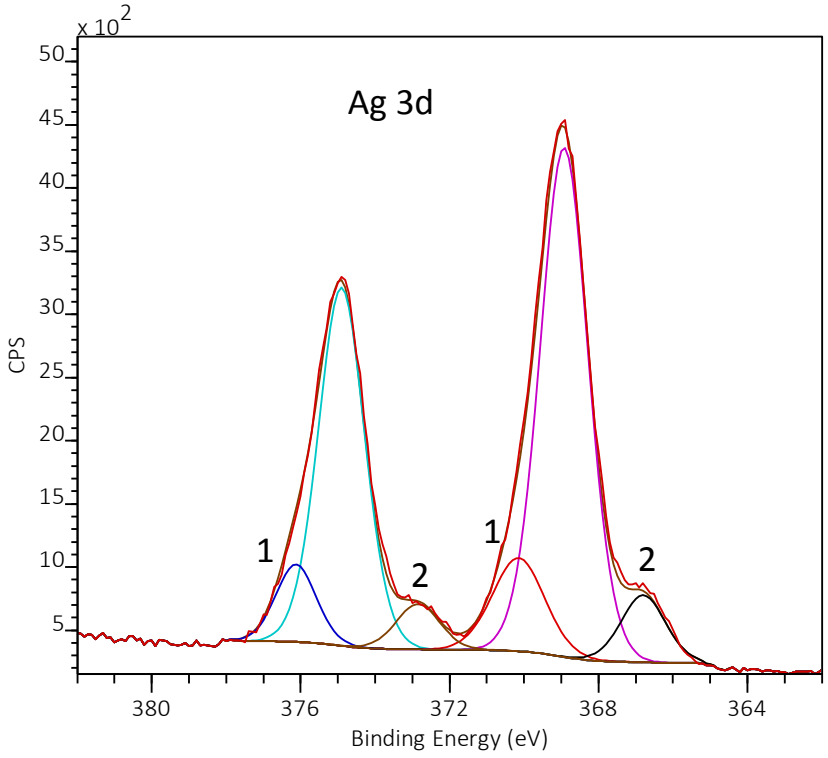


Fig. 6.9.2. Ag 3d region with three components – 1 & 2 from $Ag_2S_2O_7$ and the middle from Ag_2SO_4

7. Analysis of the calibrated XPS spectra for four important reference systems (Ag, Ag_2O, AgO, Cu).

Silver. Ag 3d bands of ion-sputtered silver surface appear at 374.4 eV (Ag $3d_{3/2}$) and 368.4 eV (Ag $3d_{5/2}$). The Ag $3d_{5/2}$ values are in good agreement with those reported by Kaushik[2] (368.3 eV) and other groups (368.0-368.3 eV)[3,4,5].
Silver (I) oxide. BE values of Ag 3d electrons in Ag_2O are consistently lower than in metallic Ag – 373.9 eV (Ag $3d_{3/2}$) and 367.9 eV (Ag $3d_{5/2}$). Similar values have been reported previously (Ag $3d_{5/2}$: 367.7-367.9 eV)[2,4,5,6,7,8]. The O 1s region can be resolved into two components. The component centred at 529.4 eV is attributed to Ag_2O and the one at 531.0 eV originates from Ag_2CO_3 contamination [6,8,9].
Silver (I,III) oxide. The Ag 3d region shows even further negative BE shift and broadening of bands as compared to Ag_2O. Since the broadening is attributed to the presence of two oxidation states of silver, the peaks were deconvoluted into two components. The higher-BE component is assigned to Ag^+ ions and the lower-BE component – to Ag^{3+} ions[10]. They are separated by 0.6-0.7 eV, which is in good agreement with previously reported results from AgO surfaces obtained electrochemically[10]. These two components should be have the same relative intensity for stoichiometric AgO, but the peak assigned to Ag(III) (shoulder) is in fact *ca.* 5 times less intense than that of Ag(I) (main peak). Ag(III) is a strong oxidizer and some of it is scavenged by carbon surface contaminants; self-decomposition of AgO in the UHV conditions[11] also contributes to decrease of Ag(III) content at the surface.
The O 1s band is made up of three components. The component at 528.6 eV is the most prominent and can be attributed to O atoms in AgO[4,6,10,12,13]. A broad peak at 530.5 eV is assumed to come from carbonate contaminant[6,12,13]. The origin of the smallest component (532.1 eV) is not certain – it can be assigned either to dissolved subsurface oxygen or to hydrogenated oxygen species on the surface[6,8,9,12].

	Ag $3d_{5/2}$	**Ag $3d_{3/2}$**	**O 1s**	**Ag $3d_{5/2}$ ref.[2]**
Ag	368.4	374.4	-	368.3
Ag_2O	367.9	373.9	529.4	367.9
AgO	367.7 (Ag^{I}) 367.0 (Ag^{III})	373.6 (Ag^{I}) 373.0 (Ag^{III})	528.6	367.5

Table 1. Comparison of BEs (in eV) for Ag, Ag_2O and AgO. All values were referenced to the C 1s line of inadvertent carbon contamination (284.6 eV).

Copper. The Cu $2p_{3/2}$ band of ion-sputtered copper surface appears at 932.92 eV and it is in good agreement with the values reported in the literature (932.2–933.1)[16] with the value of 932.62 eV usually taken as the most reliable reference value[17].

8. The values of S 2s, S2p, and O1s BEs for selected systems.

Silver (I) sulfate. The S 2p band is composed of two components due to spin-orbit splitting: 169.4 eV (S $2p_{1/2}$) and 168.2 eV (S $2p_{3/2}$). The O 1s peak appears at 531.4 eV with a shoulder at 532.4 eV. This broadening may be caused by the presence of several non-equivalent oxygen sites in the structure of Ag_2SO_4[18] or by the presence of SO_3^{2-} ions at the surface due to the previously mentioned oxygen deficiency.

Silver (I) hydrogen sulfate. The S 2p and O 1s bands appear at higher (by 0.5-0.6 eV) BEs than in the sulfate. This can be attributed to the fact that HSO_4^- anion has a less negative net charge than SO_4^{2-} anion. The O 1s band is also broader for $AgHSO_4$ (fwhm 2.5 eV; Ag_2SO_4: 2.0 eV), which may be caused by static disorder of anionic sublattice, the presence of hydrogen bonds leading to a stronger dispersion of electronic bands associated with O,[19] or by the presence of traces of H_2SO_4.

Silver (I) triflate (trifluoromethanesulfonate). The S 2p BEs are, on the other hand, very similar to those of Ag_2SO_4: 169.5 eV (S $2p_{1/2}$) and 168.3 eV (S $2p_{3/2}$). The O 1s band (532.2 eV) is symmetrical and quite narrow (fwhm 1.4 eV).

Silver (I) fluorosulfate (ESI 6.6). The S 2p bands appear at 167.9 eV (S $2p_{1/2}$) and 166.7 eV (S $2p_{3/2}$), which is also lower than in the sulfate. The O 1s band is symmetrical but rather broad (fwhm 3eV), which made it impossible to reliably deconvolute this band and pin down the precise O 1s BE values for its components. Large width of the O 1s band is due to the presence of Ag_2SO_4 in the sample and also due to the fact that three crystallographically different Ag cations are present in the crystal structure of $AgSO_3F$.

We have not determined the binding energies of S 2p and O 1s bands, neither for $Ag(II)SO_4$ nor for $Ag_2S_2O_7$. The S 2p bands are relatively narrow, unspecific, and difficult to be credibly divided into any components. The O 1s bands, on the

other hand, are quite complex and asymmetric for these two compounds thus rendering interpretation very difficult; recall that even in the case of a 'pure' $Ag(I)_2SO_4$ this spectral region had more components due to diverse surface species.

	Ag $3d_{5/2}$	Ag $3d_{3/2}$	S 2s	S $2p_{3/2}$	S $2p_{1/2}$	O 1s	other	Ag $3d_{5/2}$ lit.[21]
Ag_2SO_4	368.0	374.0	232.5	168.2	169.4	532.4 531.4	-	368.0
$AgHSO_4$	368.1	374.1	233.1	168.7	169.9	532.7 531.8	-	-
$AgSO_3F$*	366.2	372.2	230.9	166.7	167.9	*ND*	F 1s: 686.8	-
$AgSO_3CF_3$†	368.5	374.5	232.5	168.3	169.5	532.2	F 1s: 688.2 C 1s: 292.0	-
$AgSO_4$*	370.1	376.1	*ND*	*ND*	*ND*	*ND*	-	-
$Ag_2S_2O_7$*	369.3 365.9	375.3 371.9	*ND*	*ND*	*ND*	*ND*	-	-

Table 2. Comparison of XPS binding energies of silver compounds studied in this work. All values given in eV and referenced to C 1s line of inadvertent carbon contamination (284.6 eV), except: †F 1s line of $NaSO_3CF_3$ (688.2 eV)[20], *Ag $3d_{5/2}$ line of Ag_2SO_4 internal standard (368.0 eV). "*ND*" indicates that this particular value was not determined due to rapid decomposition processes and concomitant complexity of this spectral region.

9. Results of the DFT calculations for $Ag_2S_2O_7$, $AgSO_4$ and Ag_2SO_4.

Silver (I) disulfate.

```
============================================================
   Atomic Populations (Mulliken)
   -----------------------------
Species  Ion     s      p      d      f     Total  Charge (e)
============================================================
 O        1    1.87   5.01   0.00   0.00   6.87    -0.87
 O        2    1.88   4.98   0.00   0.00   6.85    -0.85
 O        3    1.87   5.01   0.00   0.00   6.88    -0.88
 O        4    1.84   4.97   0.00   0.00   6.81    -0.81
 O        5    1.89   4.93   0.00   0.00   6.82    -0.82
 O        6    1.89   4.89   0.00   0.00   6.78    -0.78
 O        7    1.87   4.97   0.00   0.00   6.84    -0.84
 O        8    1.87   5.01   0.00   0.00   6.87    -0.87
 O        9    1.88   4.98   0.00   0.00   6.85    -0.85
 O       10    1.87   5.01   0.00   0.00   6.88    -0.88
 O       11    1.84   4.97   0.00   0.00   6.81    -0.81
 O       12    1.89   4.93   0.00   0.00   6.82    -0.82
 O       13    1.89   4.89   0.00   0.00   6.78    -0.78
 O       14    1.87   4.97   0.00   0.00   6.84    -0.84
 S        1    1.13   2.51   0.00   0.00   3.65     2.35
 S        2    1.21   2.57   0.00   0.00   3.79     2.21
 S        3    1.13   2.51   0.00   0.00   3.65     2.35
 S        4    1.21   2.57   0.00   0.00   3.79     2.21
 Ag       1    0.22   0.18   9.94   0.00  10.34     0.66
 Ag       2    0.22   0.17   9.97   0.00  10.36     0.64
 Ag       3    0.22   0.18   9.94   0.00  10.34     0.66
 Ag       4    0.22   0.17   9.97   0.00  10.36     0.64
============================================================
   Bond                Population     Length (A)
============================================================
  O 001 -- Ag 001          0.16        2.31361
  O 013 -- Ag 001          0.12        2.33280
  O 002 -- Ag 001          0.08        2.41995
  O 012 -- Ag 001          0.11        2.47318
  O 007 -- Ag 001          0.07        2.47759
  O 009 -- Ag 001          0.05        2.50050
  O 006 -- Ag 002          0.09        2.41712
  O 010 -- Ag 002          0.15        2.50824
```

O 007 --	Ag 002	0.10	2.58316
O 003 --	Ag 002	0.09	2.66211
O 009 --	Ag 002	0.04	2.75051
O 012 --	Ag 002	0.05	2.80995
O 008 --	Ag 002	0.03	2.86729
O 001 --	Ag 002	0.00	2.94564

Silver (II) sulfate.

Atomic Populations (Mulliken)

Species	Ion	s	p	d	f	Total	Charge (e)
O	1	1.88	4.94	0.00	0.00	6.81	-0.81
O	2	1.86	4.98	0.00	0.00	6.84	-0.84
O	3	1.87	4.95	0.00	0.00	6.81	-0.81
O	4	1.86	4.96	0.00	0.00	6.82	-0.82
O	5	1.86	4.95	0.00	0.00	6.81	-0.81
O	6	1.88	4.94	0.00	0.00	6.82	-0.82
O	7	1.88	4.93	0.00	0.00	6.81	-0.81
O	8	1.87	4.97	0.00	0.00	6.84	-0.84
O	9	1.88	4.94	0.00	0.00	6.81	-0.81
O	10	1.86	4.98	0.00	0.00	6.84	-0.84
O	11	1.87	4.95	0.00	0.00	6.81	-0.81
O	12	1.86	4.96	0.00	0.00	6.82	-0.82
O	13	1.86	4.95	0.00	0.00	6.81	-0.81
O	14	1.88	4.94	0.00	0.00	6.82	-0.82
O	15	1.88	4.93	0.00	0.00	6.81	-0.81
O	16	1.87	4.97	0.00	0.00	6.84	-0.84
O	17	1.88	4.94	0.00	0.00	6.81	-0.81
O	18	1.86	4.98	0.00	0.00	6.84	-0.84
O	19	1.87	4.95	0.00	0.00	6.81	-0.81
O	20	1.86	4.96	0.00	0.00	6.82	-0.82
O	21	1.86	4.95	0.00	0.00	6.81	-0.81
O	22	1.88	4.94	0.00	0.00	6.82	-0.82
O	23	1.88	4.93	0.00	0.00	6.81	-0.81
O	24	1.87	4.97	0.00	0.00	6.84	-0.84
O	25	1.88	4.94	0.00	0.00	6.81	-0.81
O	26	1.86	4.98	0.00	0.00	6.84	-0.84
O	27	1.87	4.95	0.00	0.00	6.81	-0.81
O	28	1.86	4.96	0.00	0.00	6.82	-0.82
O	29	1.86	4.95	0.00	0.00	6.81	-0.81
O	30	1.88	4.94	0.00	0.00	6.82	-0.82
O	31	1.88	4.93	0.00	0.00	6.81	-0.81
O	32	1.87	4.97	0.00	0.00	6.84	-0.84
S	1	1.14	2.54	0.00	0.00	3.68	2.32
S	2	1.15	2.54	0.00	0.00	3.69	2.31
S	3	1.14	2.54	0.00	0.00	3.68	2.32
S	4	1.15	2.54	0.00	0.00	3.69	2.31
S	5	1.14	2.54	0.00	0.00	3.68	2.32
S	6	1.15	2.54	0.00	0.00	3.69	2.31
S	7	1.14	2.54	0.00	0.00	3.68	2.32
S	8	1.15	2.54	0.00	0.00	3.69	2.31
Ag	**1**	**0.33**	**0.15**	**9.54**	**0.00**	**10.02**	**0.98**
Ag	2	0.33	0.15	9.54	0.00	10.02	0.98
Ag	**3**	**0.36**	**0.16**	**9.58**	**0.00**	**10.10**	**0.90**
Ag	4	0.36	0.16	9.58	0.00	10.10	0.90
Ag	**5**	**0.36**	**0.17**	**9.47**	**0.00**	**10.00**	**1.00**
Ag	6	0.36	0.17	9.47	0.00	10.00	1.00
Ag	**7**	**0.35**	**0.18**	**9.47**	**0.00**	**10.00**	**1.00**
Ag	8	0.35	0.18	9.47	0.00	10.00	1.00

Bond		Population	Length (A)
O 019 --	**Ag 001**	**0.20**	**2.05184**
O 003 --	**Ag 001**	**0.20**	**2.05184**
O 006 --	**Ag 001**	**0.15**	**2.16218**
O 022 --	**Ag 001**	**0.15**	**2.16218**
O 008 --	**Ag 001**	**0.02**	**2.90177**
O 024 --	**Ag 001**	**0.02**	**2.90177**
O 011 --	Ag 002	0.20	2.05184
O 027 --	Ag 002	0.20	2.05184
O 014 --	Ag 002	0.15	2.16218
O 030 --	Ag 002	0.15	2.16218
O 016 --	Ag 002	0.02	2.90177
O 032 --	Ag 002	0.02	2.90177
O 026 --	**Ag 003**	**0.20**	**2.06671**
O 010 --	**Ag 003**	**0.20**	**2.06671**
O 015 --	**Ag 003**	**0.16**	**2.18564**
O 031 --	**Ag 003**	**0.16**	**2.18564**
O 001 --	**Ag 003**	**0.02**	**2.97123**
O 001 --	**Ag 003**	**0.02**	**2.97123**
O 018 --	Ag 004	0.20	2.06671
O 002 --	Ag 004	0.20	2.06671
O 007 --	Ag 004	0.16	2.18564
O 023 --	Ag 004	0.16	2.18564
O 007 --	Ag 004	0.02	2.97123
O 007 --	Ag 004	0.02	2.97123
O 005 --	**Ag 005**	**0.21**	**2.06109**
O 021 --	**Ag 005**	**0.21**	**2.06109**
O 032 --	**Ag 005**	**0.22**	**2.13337**
O 016 --	**Ag 005**	**0.22**	**2.13337**
O 001 --	**Ag 005**	**0.04**	**2.99744**
O 017 --	**Ag 005**	**0.04**	**2.99744**
O 013 --	Ag 006	0.21	2.06109
O 029 --	Ag 006	0.21	2.06109
O 024 --	Ag 006	0.22	2.13337
O 008 --	Ag 006	0.22	2.13337
O 025 --	Ag 006	0.04	2.99744
O 009 --	Ag 006	0.04	2.99744
O 020 --	**Ag 007**	**0.21**	**2.05707**
O 004 --	**Ag 007**	**0.21**	**2.05707**
O 025 --	**Ag 007**	**0.20**	**2.13692**
O 009 --	**Ag 007**	**0.20**	**2.13692**
O 007 --	**Ag 007**	**0.02**	**2.97089**
O 023 --	**Ag 007**	**0.02**	**2.97089**
O 010 --	**Ag 007**	**0.00**	**2.99442**
O 026 --	**Ag 007**	**0.00**	**2.99442**
O 028 --	Ag 008	0.21	2.05707
O 012 --	Ag 008	0.21	2.05707
O 017 --	Ag 008	0.20	2.13692
O 001 --	Ag 008	0.20	2.13692
O 015 --	Ag 008	0.02	2.97089
O 031 --	Ag 008	0.02	2.97089
O 018 --	Ag 008	0.00	2.99442
O 002 --	Ag 008	0.00	2.99442

Silver (I) sulfate.

Atomic Populations (Mulliken)

Species	Ion	s	p	d	f	Total	Charge (e)

O	1	1.86	4.98	0.00	0.00	6.84	-0.84
O	2	1.86	4.98	0.00	0.00	6.84	-0.84
O	3	1.86	4.98	0.00	0.00	6.84	-0.84
O	4	1.86	4.98	0.00	0.00	6.84	-0.84
O	5	1.86	4.98	0.00	0.00	6.84	-0.84
O	6	1.86	4.98	0.00	0.00	6.84	-0.84
O	7	1.86	4.98	0.00	0.00	6.84	-0.84
O	8	1.86	4.98	0.00	0.00	6.84	-0.84
S	1	1.16	2.56	0.00	0.00	3.72	2.28
S	2	1.16	2.56	0.00	0.00	3.72	2.28
Ag	1	0.26	0.25	9.94	0.00	10.45	0.55
Ag	2	0.26	0.25	9.94	0.00	10.45	0.55
Ag	3	0.26	0.25	9.94	0.00	10.45	0.55
Ag	4	0.26	0.25	9.94	0.00	10.45	0.55

==========

Bond	Population	Length (A)
O 007 -- Ag 001	**0.16**	**2.39348**
O 008 -- Ag 001	**0.16**	**2.39348**
O 004 -- Ag 001	**0.11**	**2.43677**
O 004 -- Ag 001	**0.11**	**2.43677**
O 001 -- Ag 001	**0.05**	**2.66244**
O 002 -- Ag 001	**0.05**	**2.66244**

==========

Estimate of Madelung potential at various Ag sites.

Using the classical expression for electric potential created by a point charge *Q*, at a distance *r* from the charge, and taking only the first coordination sphere into account (up to 3 Å), one gets the following values of Madelung shifts of the BEs at Ag sites:

Silver (I) disulfate.

Ag1=Ag3 –30.05 eV
Ag2=Ag4 –36.67 eV

hence the difference between the two is **6.62 eV**. This value should be compared to the experimental one of 3.4 eV, which reflects not only the Madelung potential differences at diverse Ag sties, but also other contributions. The agreement is not bad overal, while keeping in mind the very crude approximation applied here to Coulombic effects in the crystal (*i.e.* only the first coordination sphere of a metal has been taken into account). Indeed, the impactof the first negatively charged coordination sphere around Ag(I) sites should be somewhat moderated by the second one (positively charged), etc.

Silver (II) sulfate.

Ag1=Ag2 –30.84 eV
Ag3=Ag4 –30.44 eV
Ag5=Ag6 –30.65 eV
Ag7=Ag8 –29.61 eV

Average value: **–30.39 eV** (averaging is performed since the peak seen in experimental spectrum is very broad).

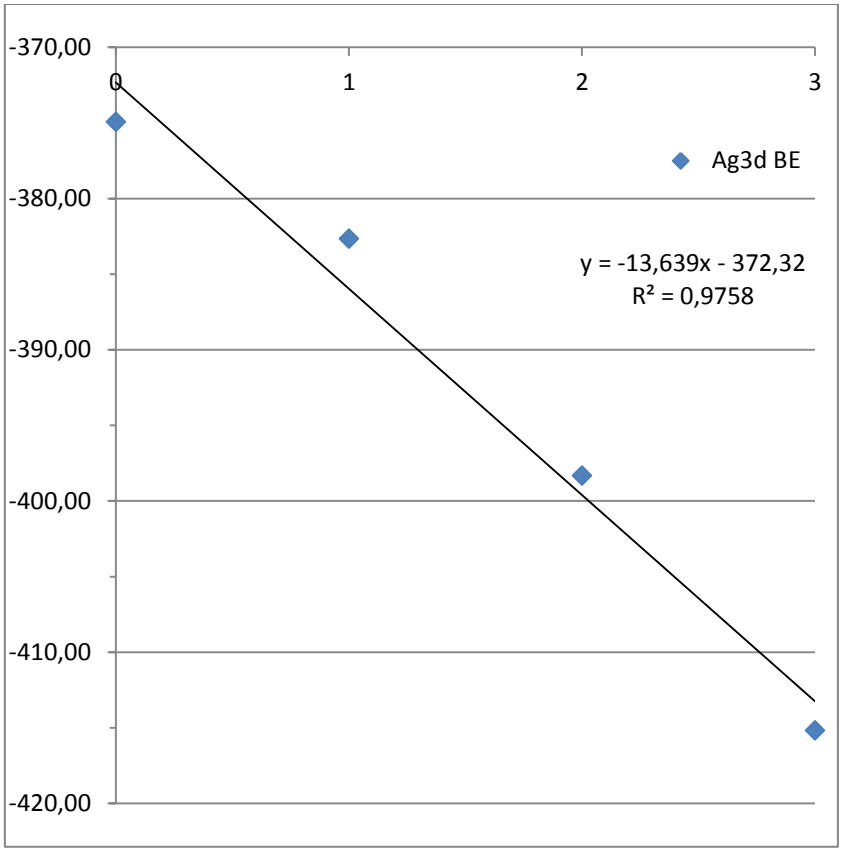
Silver (I) sulfate.

Ag1=Ag2=Ag3=Ag4 –29.32 eV

Ag $3d_{5/2}$ BEs for isolated silver (0), (I), (II) and (III) species in the gas phase (B3LYP, all-electron ANO-RCC basis set, as computed with Gaussian'09).

Ag(0) –374.94 eV
Ag(I) –382.67 eV
Ag(II) –398.34 eV
Ag(III) –415.18 eV

hence the shift related to the increase of the oxidation state equals, on average, **–13.6** eV/oxidation state unit as obtained from linear extrapolation between Ag(0) and Ag(III) – see figure below.



This average value may now be applied to estimate the BE shift with the increasing ionicity of the Ag-O bonds (Ag_2SO_4→$Ag_2S_2O_7$) as well as with the increasing oxidation state of silver (Ag_2SO_4→$AgSO_4$).
The Mulliken charge on Ag site increases slightly, from +0.55e for Ag_2SO_4, to +(0.64–0.66)e for $Ag_2S_2O_7$. This ~0.1e charge difference corresponds to a *ca.* 1.4 eV difference of BEs induced purely by on-site charge on silver center.
On the other hand, charge difference is much larger for the Ag_2SO_4 (+0.55e) & Ag(II)SO_4 (+0.90e via +0.98e to +1.00e) pair. The 0.35-0.45e difference corresponds to as much as 4.8–6.1 eV BE difference.

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