Supplementary materials

Formation of Nanoclusters in Gold Nucleation

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1. AUC raw data

The AUC raw data of the AUC band forming experiment at 510 nm are shown in Figure S1.

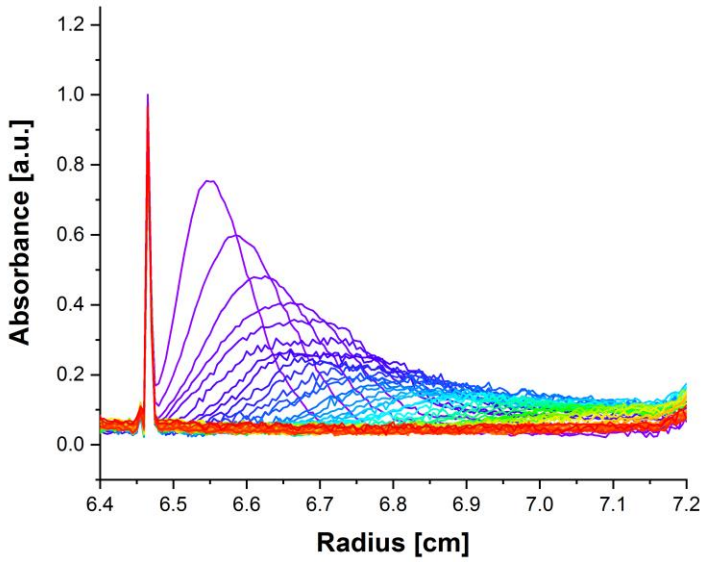

Figure S1: AUC raw data at 510 nm of a band forming experiment, where gold clusters were formed.

2. SEDFIT Analysis of experiments B-G

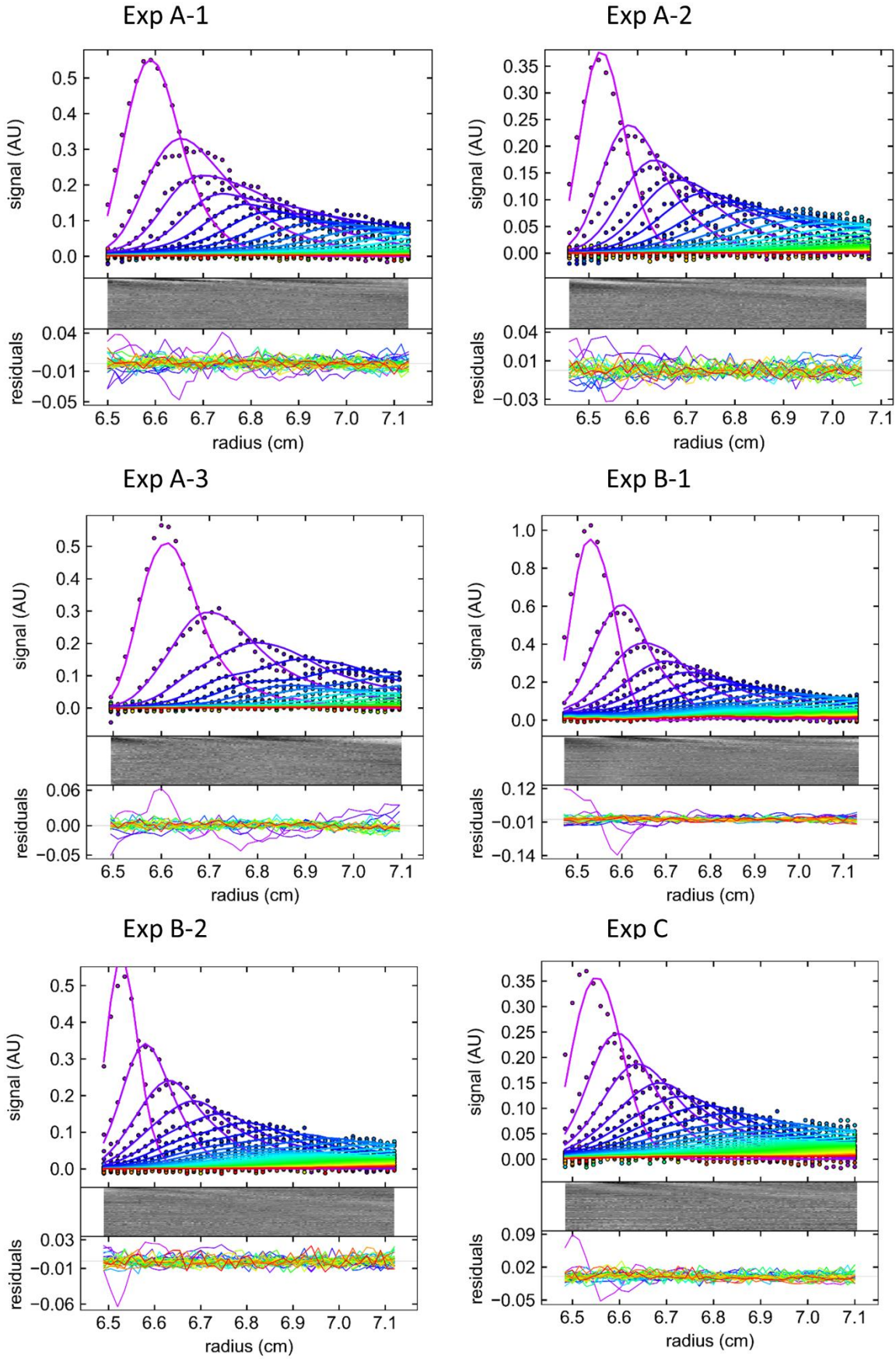

Figure S2: Corresponding fits to the c(s) analysis in SEDFIT of experiments A-C. The RMSD values are between 0.0065 and 0.0091.

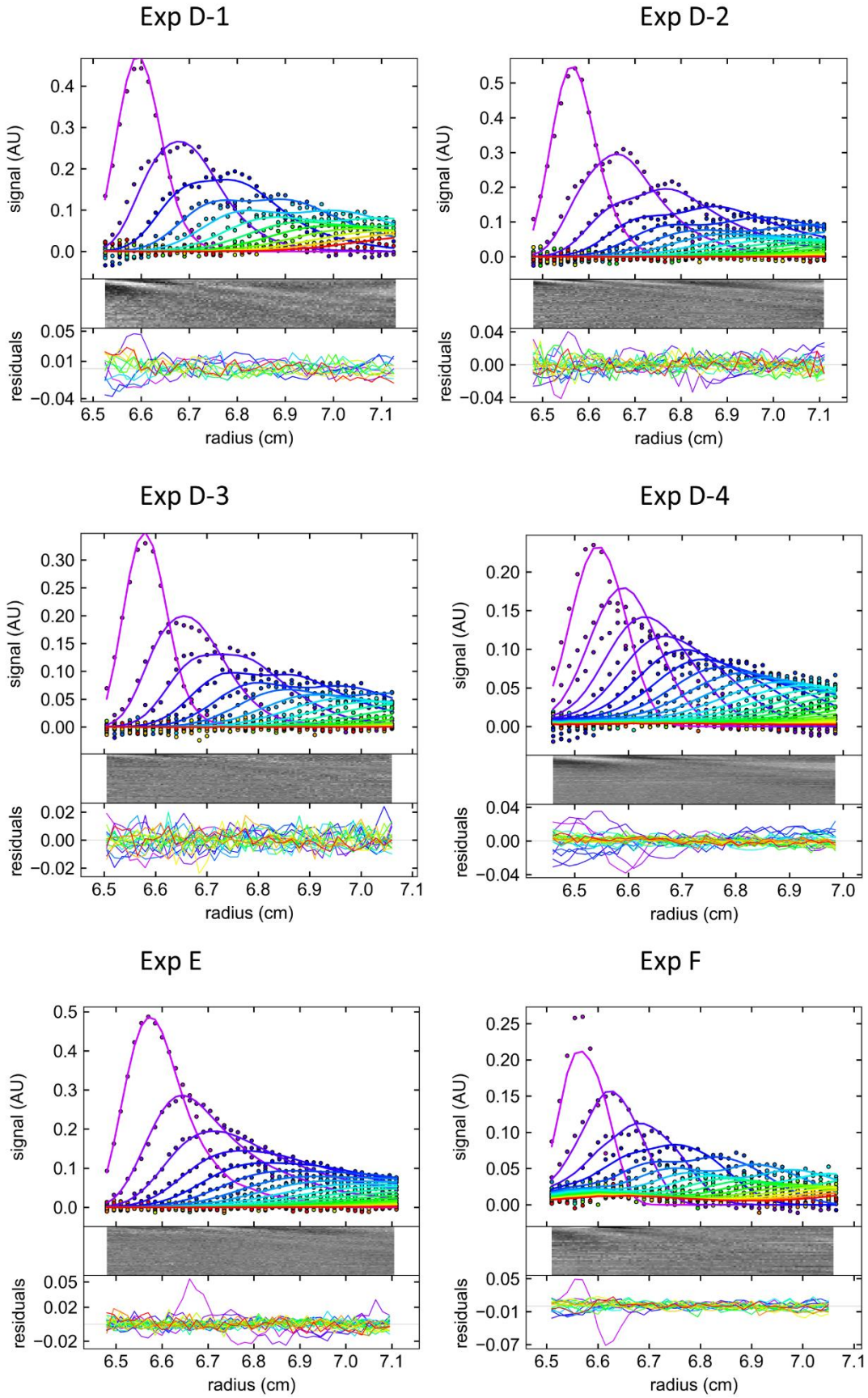

Figure S3: Corresponding fits to the c(s) analysis in SEDFIT of experiments D-F. The RMSD values are between 0.0063 and 0.0105.

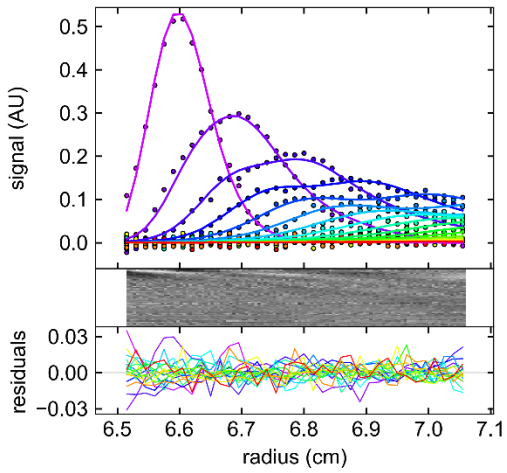

Figure S4: Corresponding fits to the c(s) analysis in SEDFIT of experiments G. The RMSD value is 0.0083.

Analysis of the AUC raw data at 510 nm of experiments B-G was performed using the analysis software SEDFIT.

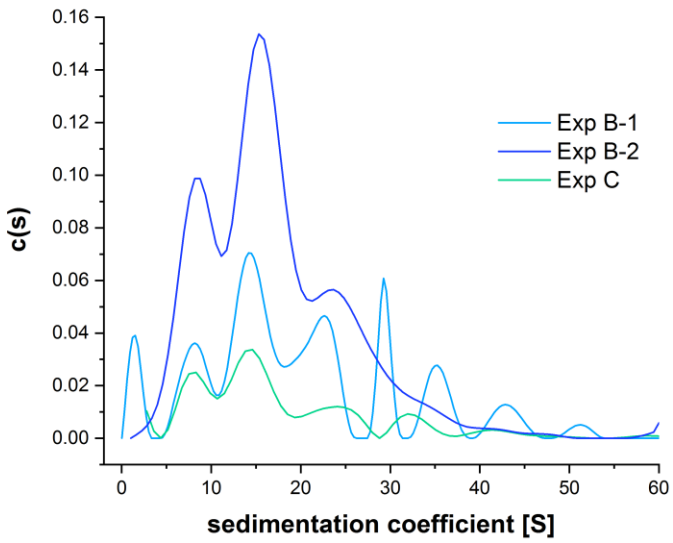

Figure S5: Analysis of experiments B (with one repetition) and C. Shown is the c(s) distribution which exhibits different cluster species. In experiment B the same equivalents as in experiment A were used, in experiment C the concentration of $NaBH_4$ was varied.

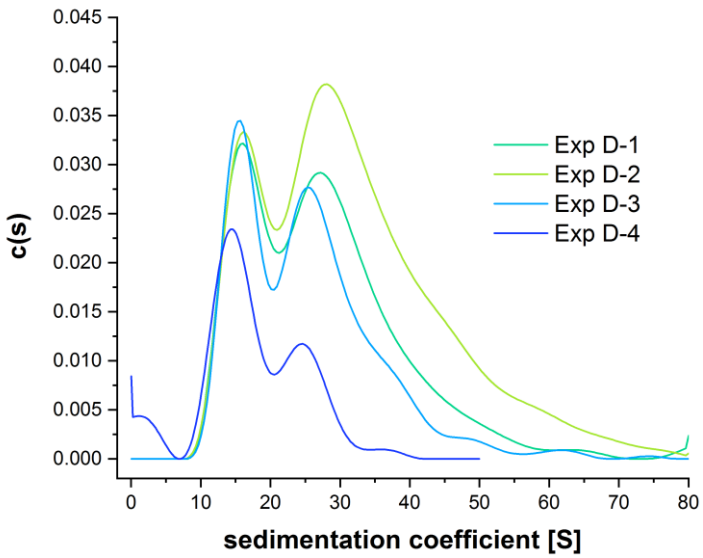

Figure S6: Analysis of the experiment D (with three repetitions). Two different cluster species seem to appear in every distribution. The gold concentration was varied compared to experiment A.

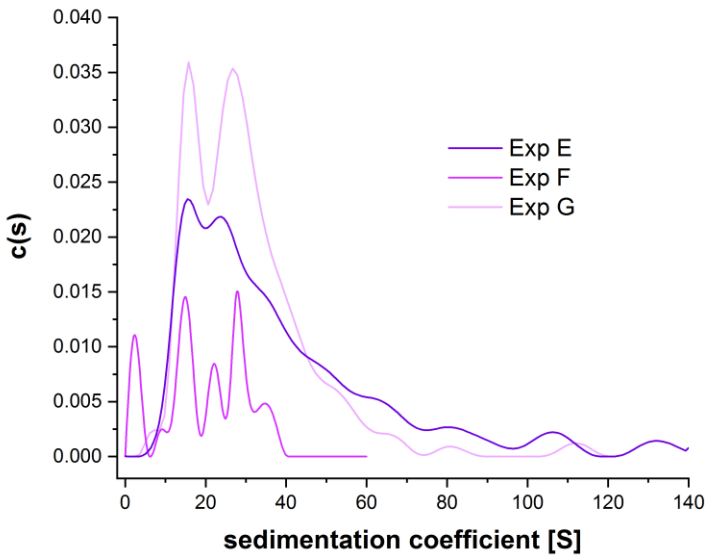

Figure S7: Analysis of the experiment E,F and G. In experiment E and F also the gold concentration was varied, in experiment G the concentration of the stabilizer thioglycerol was varied.

3. ULTRASCAN Analysis of experiments A and C

Multiwavelength analysis using ULTRASCAN was performed on Experiment A-1, A-3 and experiment C. For the analysis, the tool PCSA-HL was used and provided the following results for representative wavelengths of experiment A-3, showing a plot of the sedimentation coefficient against $\bar{v}$, which were the values fitted for, for some representative wavelengths.

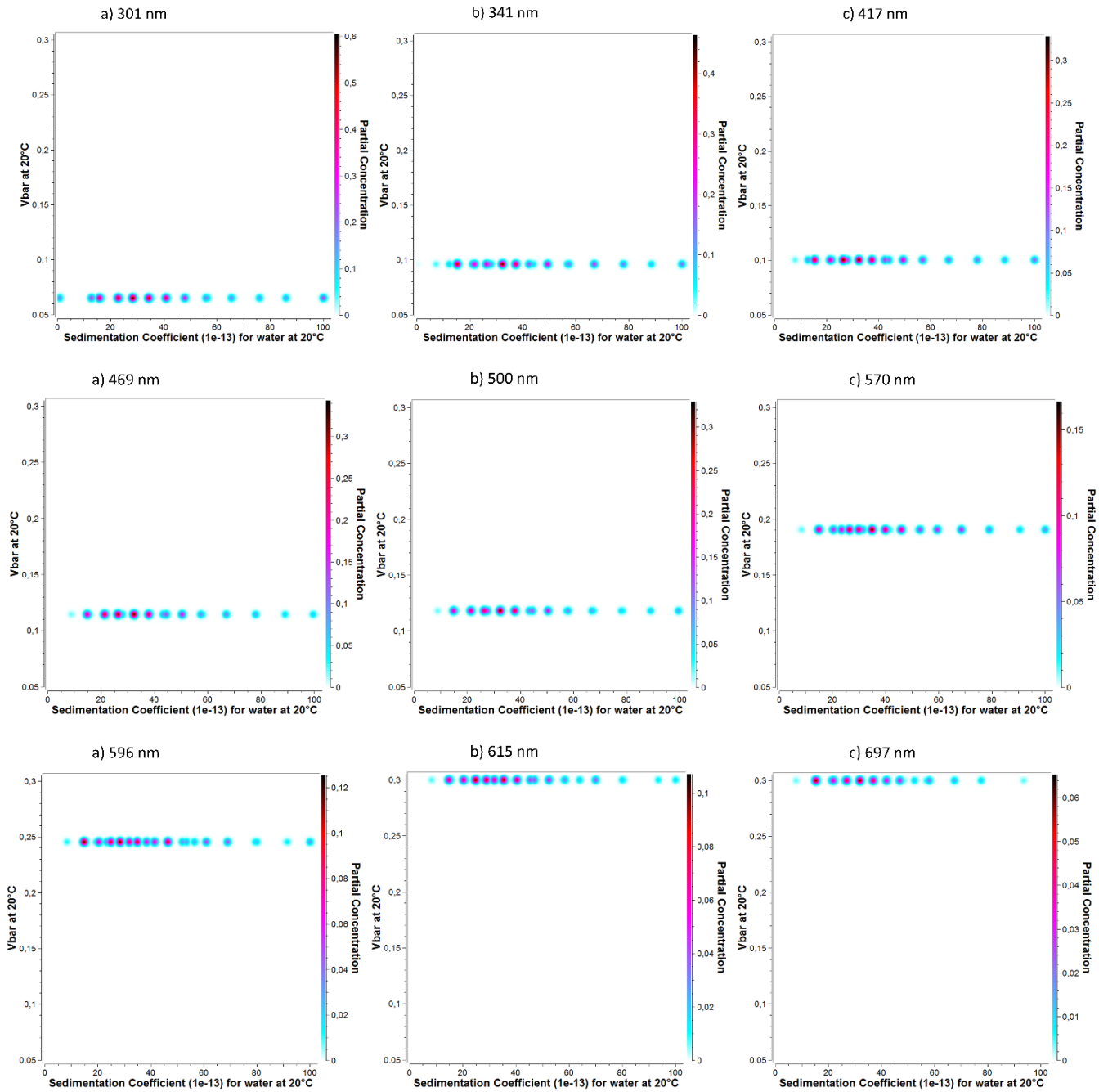

Figure S8: Analysis of a band forming experiment, where gold clusters where formed, with ULTRASCAN. Shown are the fits for the sedimentation coefficient and $\bar{v}$ for representative wavelengths of experiment A-3.

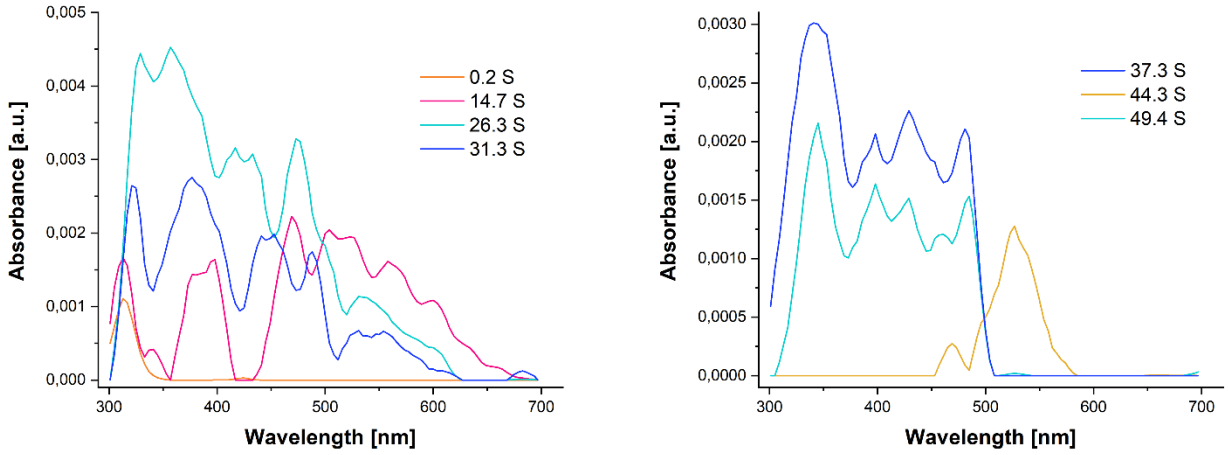

Figure S9: Individual UV/Vis spectra extracted from the PCSA MWL analysis for each species. For better overview they were separated in two different graphs.

The 3D plots of the MWL analysis of the experiments A-1 and C are shown in Figure S10 and S11.

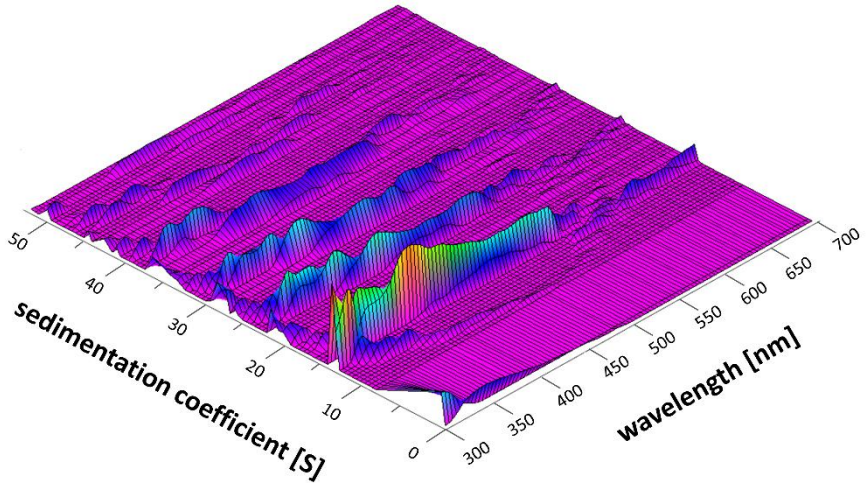

Figure S10: 3D plot of the multiwavelength analysis of experiment A-1 of a band forming experiment of gold clusters. The species are plotted versus the wavelength.

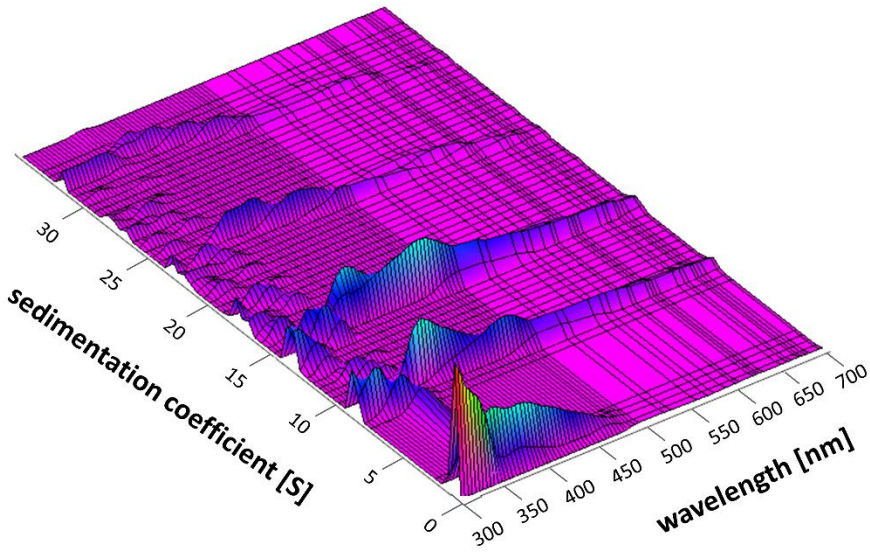

Figure S11: 3D plot of the multiwavelength analysis of exp C of a band forming experiment of gold clusters. The species are plotted versus the wavelength.

4. Overview of the species from analysis

All the species found in the SEDFIT and ULTRASCAN analysis of the different experiments are listed in Table S1. The left column gives the mean s value of clusters found in different analyses, which are the same species. The value Ω gives the statistical significance and σ the standard deviation.

Table S1: Overview of all the species found in analysis of band forming experiments of gold clusters in AUC. Shown are all the species found for SEDFIT analysis at 510 nm of each experiment and the species found in MWL analysis in ULTRASCAN of exp A-1, A-3 and C.

			A-1	**A-2**	**A-3**	**B-1**	**B-2**	**C**	**D-1**	**D-2**	**D-3**	**D-4**	**E**	**F**	**G**	**A-1**	**A-3**	**C**
s	**σ**	**Ω***	**SEDFIT Sedimentation coefficient [S]**													**ULTRASCAN Sed. coefficient [S]**		
0.2	0.00	2														0.2	0.2	
1.3	0.04	3				1.2						1.3						1.3
2.3	0.15	2	2.4											2.1				
5.6	0.00	1			5.6													
7.6	0.30	2				7.9									7.3			
8.9	0.45	5	8.5				8.7	8.5						9.1				9.9
15	0.47	16	15.5	15.1	15.5	14.6	15.3	15.0	16.1	16.1	15.7	14.3	15.5	14.8	15.8	15.9	14.7	15.9
24	0.63	12	24.7	24.4	24.6	22.4	23.6	24.7			25.3	24.6	23.9	22.0		24.0		25.7
27	0.56	5							27.2	28.1				27.7	26.7		26.3	
32	0.98	7	31.4		31.7	32.7		32.7								30.5	31.3	34.3
36	0.80	4		36.5								35.9		34.7			37.3	
41	1.46	5	40.4		39.4	43.0		42.4								39.2		
45	0.69	3														45.7	44.3	44.0
50	1.72	5	50.7		49.3						48.3					54.4	49.3	
62	1.24	3	62.7		63.3			60.2										
76	1.00	2	76.6		74.6													
81	0.50	2											80.2		81.2			
88	2.35	2	90.5		85.8													
106	2.61	4	106.1		101.3								106.2		111.5			
125	0.00	1			124.5													
132	0.00	1											132.3					

All values were corrected for the same density and viscosity so they are comparable. * Statistical significance.

5. Thioglycerol

To determine the length of a thioglycerol molecule, MATERIALS STUDIO was used to draw a 3D model and to measure the length. The length is given as 4.7 Å. The 3D model is shown in Figure S12.

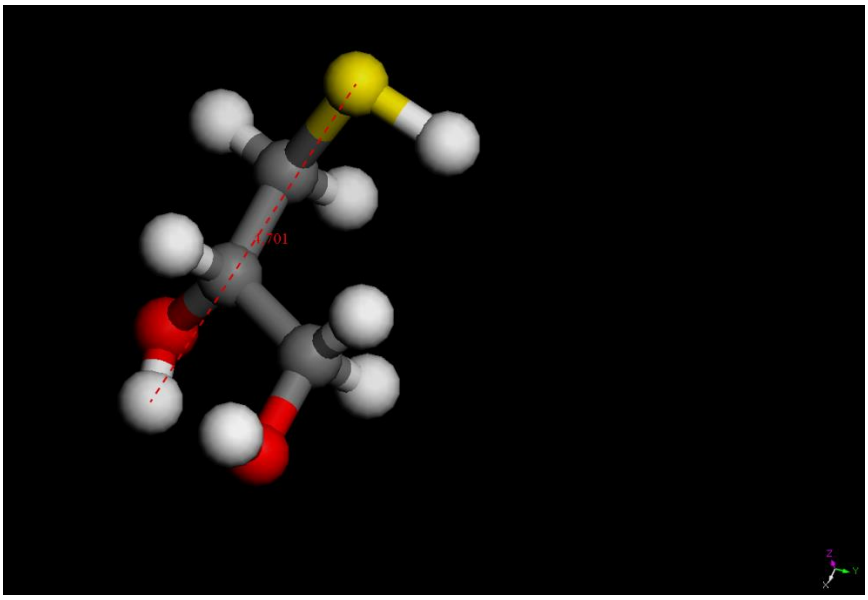

Figure S12: A 3D model of thioglycerol drawn with MATERIALS STUDIO.

6. Core-shell model for size evaluation

To calculate the size of the gold core, a core-shell model is applied. This relies on the assumption that the overall density of the particle consists proportionately of the shell density and core density, which in our case refers to the density of the gold core ρ_{core} (19.32 g/ml) and the thioglycerol shell ρ_{shell} (1.25 g/ml). The ratio is determined by the respective volume fraction of the overall particle .This relates to the radius fraction to the power of three (in case of a spherical particle) and can be also described by the following formula:

$$\bar{v}_P = r^3\left(\rho_{core} \cdot {r_{core}}^3 + \rho_{shell}(r^3 - {r_{core}}^3)\right)^{-1}$$

$\bar{v}_P$ refers to the partial specific volume of the overall particle, r to the radius of the overall particle and r_{core} to the radius of the core. The volume fraction of each component can be used to calculate the overall density. From AUC analysis of the gold clusters the sedimentation coefficient s of each cluster is determined, which can be used to calculate the radius of the overall particle with previous knowledge of the density of the overall particle $(\rho_P = {\bar{v}_P}^{-1})$ by $2r = \sqrt{\frac{18\eta_S s}{\rho_P - \rho_S}}$. In our case, the overall density is not well determined, but the fraction the shell contributes to the overall radius (0.47 nm) and density (1.25 g/ml) is known as well as the core density. Using these values and the model described above, sedimentation coefficients can be calculated under variation of the core size. The sedimentation coefficient, which matches the value obtained from analysis gives back the respective core size which applies to the evaluated particle.

This way, the core radius can be calculated based on the sedimentation coefficient of the particle, knowledge of the solvent (see Table 2), the density of the core and the density and thickness of the surfactant layer $(r_P - r_{core})$.