Supporting Information

Toward Vibrational Tomography of Citrate on Dynamically Changing Individual Silver Nanoparticles

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Keywords: silver nanoparticles, surface-enhanced Raman scattering, citrate, single-particle spectroscopy, adsorbate structure, cluster analysis

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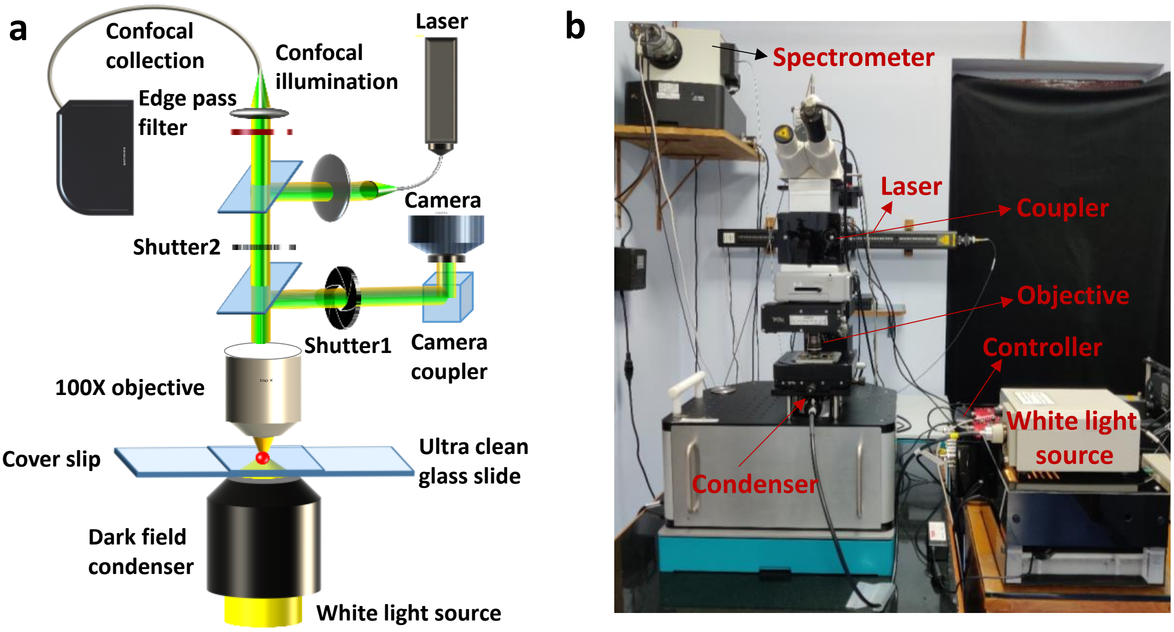

Figure S1. (a) Schematic representation of the set-up for dark field microscopy coupled with confocal Raman microspectrometer, and (b) optical photograph of the set-up presented in (a).

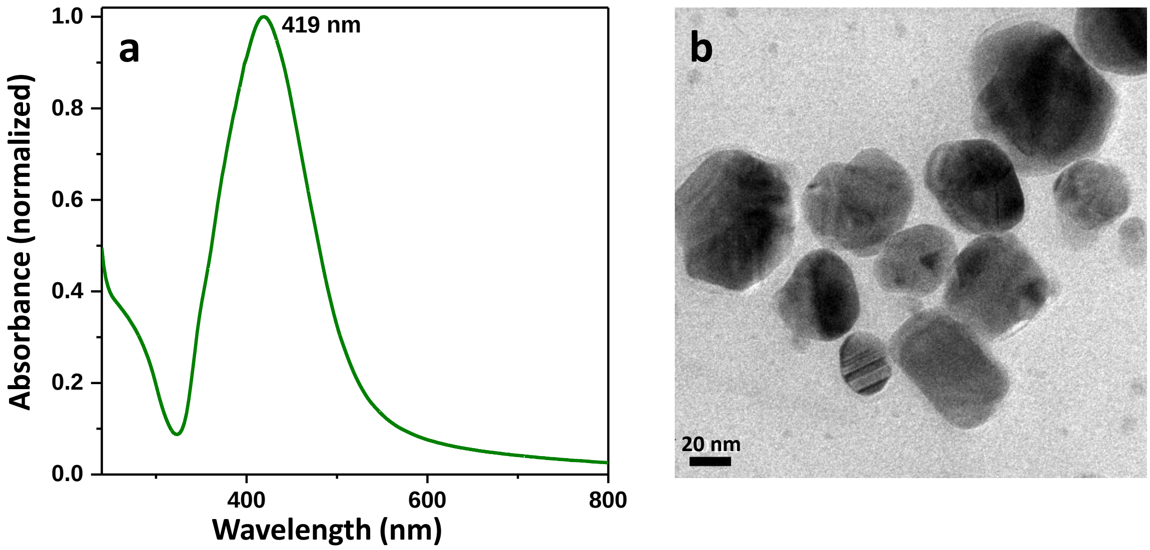

Figure S2. Characterization of citrate-capped AgNPs. (a) UV-visible absorption spectrum and (b) TEM image of as-synthesized AgNPs.

Calculation SI. Laser power incident per nanoparticle:

Average diameter (D) of AgNPs = 50 nm

Average radius (R) of AgNPs = 25 nm

Area for spherical NPs – ($A_1 = 4\pi R^2$) is 7850 nm^2

Spot size of laser beam – $A_2 = \pi r^2$ and radius of beam spot (r) = (1.22 x λ x f/d), where λ is wavelength of incident laser light (632.8 nm), f is focal length of objective (1.8 mm for 100 X objective) and d is beam diameter (1.22 mm)

r = (1.22 x 632.8 nm x 1.8 mm)/1.22 mm = 1139.04 nm or 1.14 μm

A_2 = 3.14 x 1139.04 x 1139.04 = 4.073×10^6 nm^2

Laser power at laser spot size (4.073×10^6 nm^2) was 650 μW

So, for 1 nm^2 size laser power is 159.6×10^{-6} μW

Laser power per NP (A_1 = 7850 nm^2) is 1.3 μW

Calculation SII. Laser power absorbed per nanoparticle:

Absorption/extinction efficiency (Q_{ext}) of NP, $Q_{ext} = \sigma_{eff}/\pi r^2$, where σ_{eff} is the extinction coefficient/cross-section, and r is the radius of the NP.

From UV-visible data of AgNPs, Absorbance (A) = ξcl, A = 0.532, c is concentration of NPs = 0.333×10^{-4} $molL^{-1}$, l is length of cuvette = 1 cm, thus, ξ (molar extinction coefficient) = 1.598×10^7.

$\sigma_{eff} = (\xi \times 1000 \times 2.303)/N_A = 0.611 \times 10^{-13}$, N_A is the Avogadro number.

$Q_{ext} = 7.787 \times 10^{-4}$
Laser power absorbed per NP = laser intensity x Q_{ext} = 650 μW x 7.787×10^{-4} = 0.5061 μW or ~506 nW.

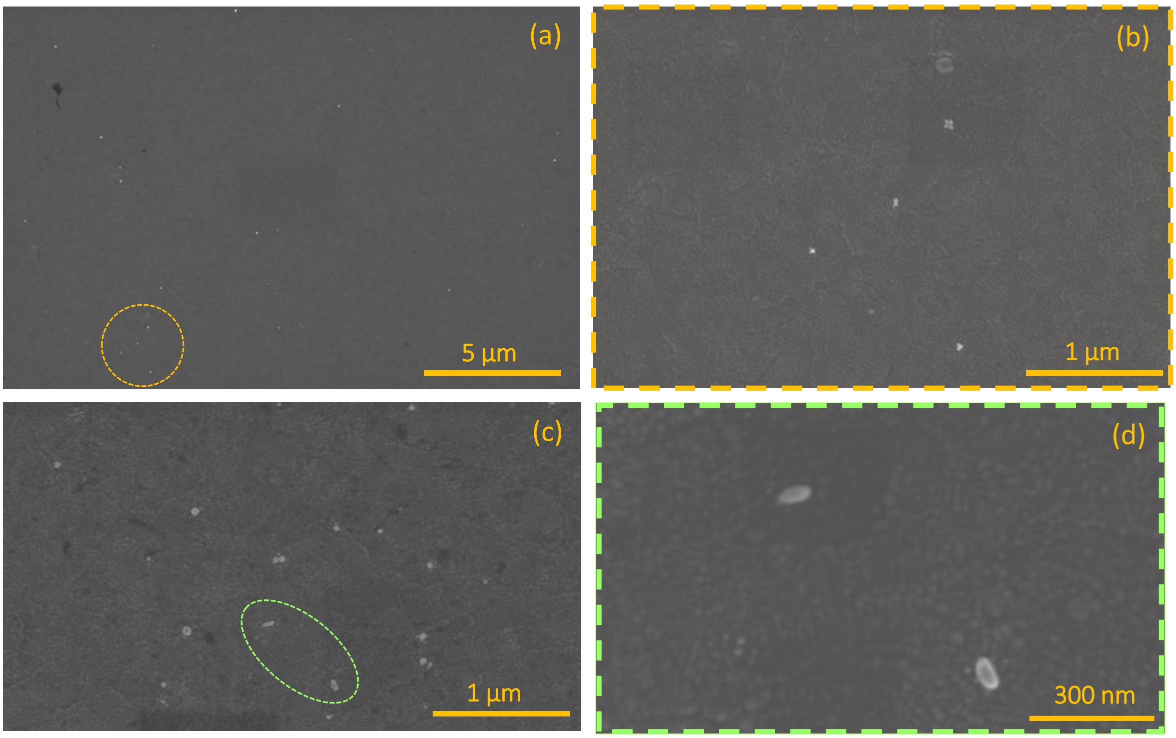

Figure S3. FESEM images of AgNPs immobilized on an ITO glass slide. (a) Large area FESEM image, (b) magnified image of the encircled area of (a), (c) another large area FESEM image with 5 times higher magnification, and (d) magnified image of the encircled area of (c).

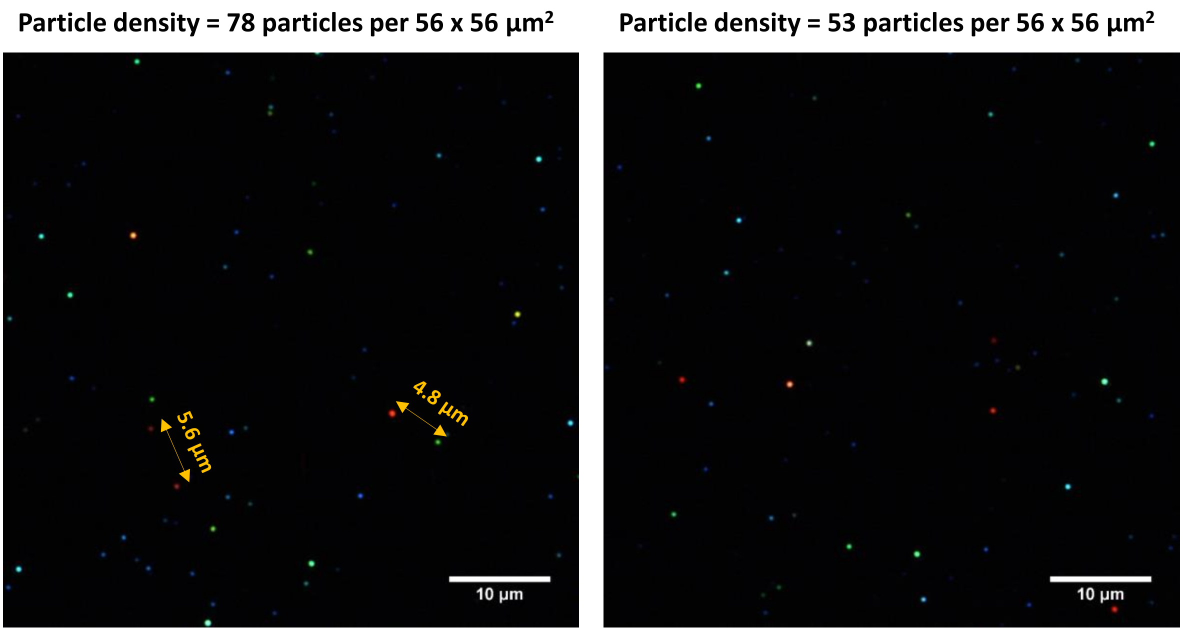

Figure S4. Particle density calculations for the immobilized AgNPs used for SP-SERS. The particle density calculations were performed using DFM images with Image J software. Inter-particle distances are also mentioned in the DFM images.

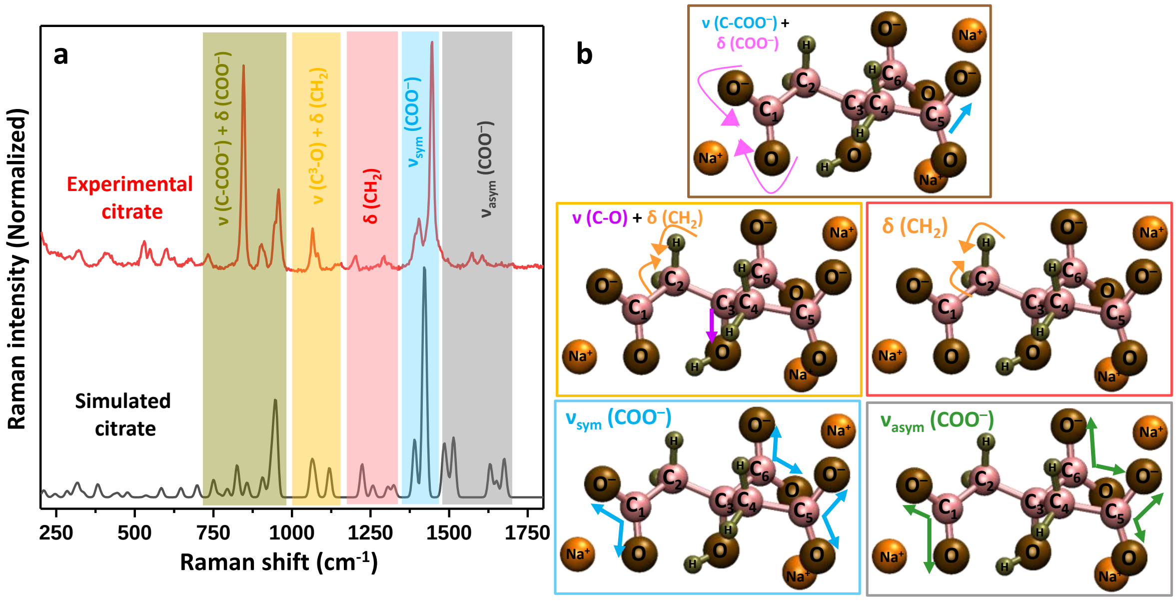

Figure S5. (a) Comparison between the experimental and DFT calculated Raman spectra of TSC (assignments of the vibrational bands are displayed vertically along with colored bands) and (b) DFT optimized structures of TSC, calculated at the B3LYP/6-31 + G(d) level. The vibrational modes of TSC are shown pictorially with arrows.

Table S1. Band assignments of SERS frequencies for distinct spectra of citrate (Figure 1b of manuscript) with the help of the simulated Raman spectrum of TSC (Figure S3a) and existing literature[1–2] on the SERS of citrate.

Frequency bands (SERS, Figure 1b) (cm^{-1})	Simulated Raman of TSC, Figure S3a (cm^{-1})	Literature[1–2] (SERS) of adsorbed citrate(cm^{-1})	Assignments
820–870	824	843	ν(C-COO⁻)+ δ(COO⁻)
930–980	948	956	ν(C-COO⁻)
1050–1100	1065, 1072	1057	ν(C-O)
1170–1330	1118, 1224, 1258	1212, 1267	$\delta(CH_2) + \gamma(CH_2) + \delta(COO^-)$
1350–1420	1390	1417	$\nu_{sym}(COO^-)$
1440–1480	1422, 1483		$\delta(CH_2)$
1560–1640	1629	1575	$\nu_{asym}(COO^-)$

Notes: ν indicates stretching, ν_{sym} is symmetric stretching, ν_{asym} is asymmetric stretching, δ is in-plane bending and rocking, γ is out-of-plane wagging and twisting.

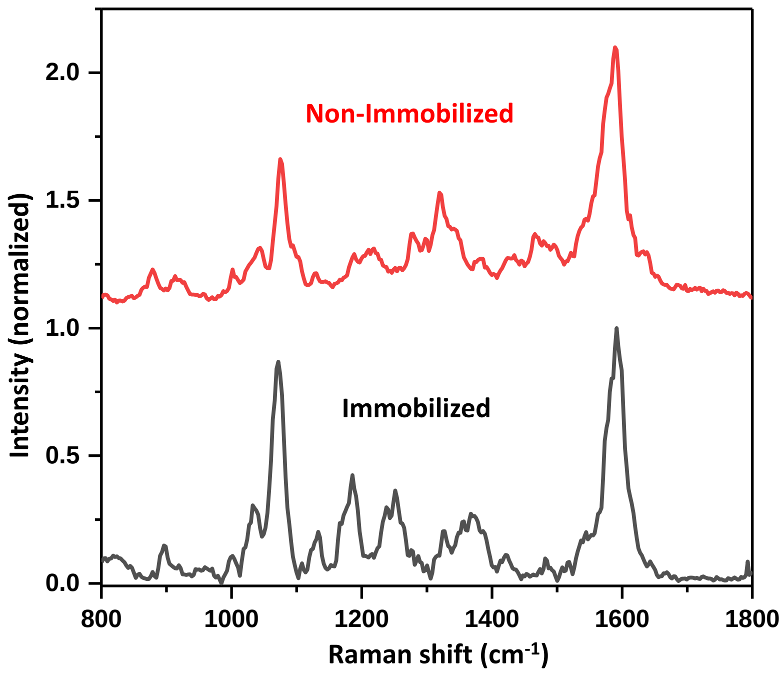

Figure S6. Comparison between SERS spectra obtained in immobilized and non-immobilized AgNPs. In both the cases, spectra were similar which indicated that spectra were due to citrate rather than MPTMS.

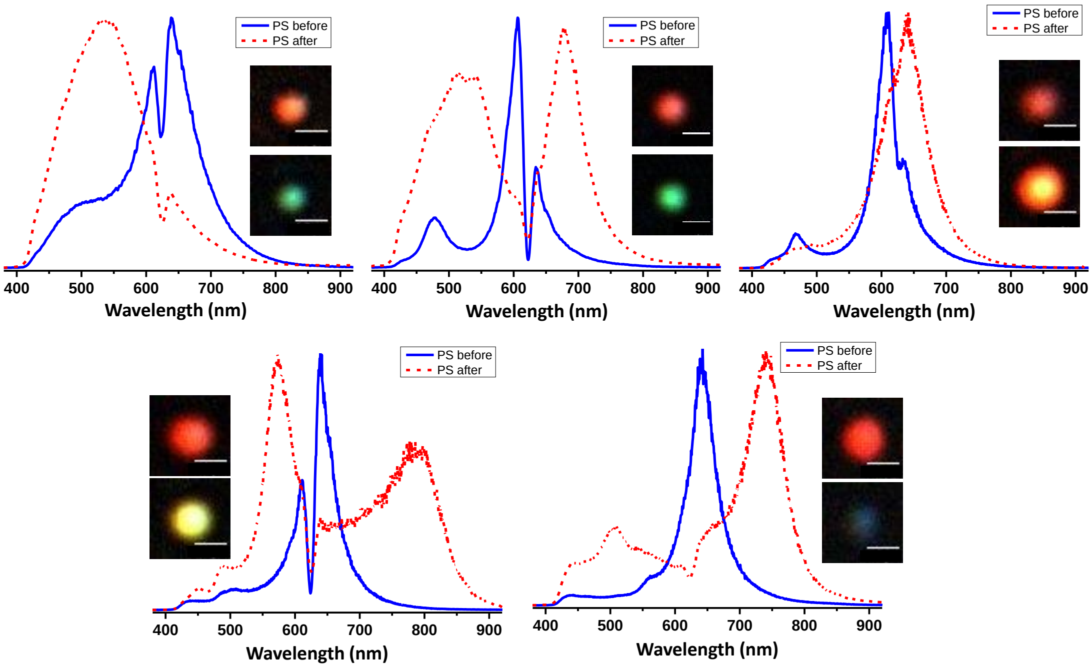

Figure S7. Plasmonic scattering spectra of single AgNPs before and after laser exposure. DFM images of the particles monitored before and after laser exposure are displayed along with their scattering spectra. Dip in peak in all spectra is due to presence of laser band pass filter in the optical path (scale bar in all DFM images is 0.5 µm).

II. Clustering methods and algorithms:

In the CA algorithm, a k-means++ algorithm[3-4] adapted from ImageJ was used to spread out the initial cluster centers (CCs). A CC is a point which is closest to the members of that cluster. In this approach, the first CC was chosen randomly among the spectral data points to be clustered. Then, remaining CCs were chosen such that the probability of the point to become a CC is dependent on its squared distance from the closest existing CC. Once the k-centers were chosen, k-means clustering algorithm was performed.

Technical terms (TT)	Brief explanation of TT	Limiting values for cluster analysis
Tolerance limit[4]	It stops the iterative process of CA when the distance between the successive points is $\leq 10^{-7}$ value.	10^{-7}
Randomization seed[4]	The seed is the initial value of the internal state of the pseudorandom number generator. It is enabled so that the cluster centers are initialized to the same values every time algorithm starts.	200
Noise threshold	It indicates S/N value and the spectra with maximum intensity ≤80 were considered as noise.	80

Step 1. All the data collected from time dependent SERS measurement was exported from Witec Raman spectrometer control software in a text format. These text files were used as input files to prepare files suitable for cluster analysis algorithm in ImageJ.[3-4] The customized MATLAB code named as *before cluster analysis* shown below (Code 1), was used to prepare data for cluster analysis. ImageJ cluster analysis algorithm was used to visualize clustering process.

Code 1: Before cluster analysis

```
clear all;
nos=1400; % number of spectra
nx=40;
ny=35;
nof=7; % number of files
start_fileno = 1;
noiselevel = 80;
noise_limit = 80; % noise limit to distinguish between noise and spectrum
x=importdata('x.txt');
raylb4=100; % Data point before which rayleigh appears <<
raylcorrect=1; % set to 1 if rayleigh needs to be corrected <<
speclen=1024; % length of spectrum <<
xzeroI=28; %array index where x is zero <<
smoothFlag = 0; %set to 1 if smoothing is required
RamanBadDataRm = 0; %set to 1 if bad data at specific points need to be removed
```

```
BadData8 = 292;
repeat_smooth = 2;
for i=start_fileno:1:(start_fileno + nof-1)
   y_temp = importdata(sprintf('y%i.txt',i));
   if i==1
      A=y_temp;
   else
      A=vertcat(A,y_temp);
   end
end
A=reshape(A,[],nos);
```

Step 2. Files generated by above program were used as input files for k-means++ and k-means algorithm in ImageJ. This step generated clustered datasets from input spectra.

Step 3. A second customized MATLAB code, named as *after cluster analysis* was used to prepare cluster analysed data for further plotting and analysis. Then these spectra were imported in Origin 2017 to plot as shown in Figure 2 and subsequent sections. The MATLAB code *after cluster analysis* code (Code 2) is given below.

Code 2: After cluster analysis

```
clear all;
nos=1400; % number of spectra
nx=40;
ny=35;
nof=7; % number of files
start_fileno = 1;
nocs=15; % number of clusters
clusters = dlmread('Clusters.txt');
centroid = dlmread('Centroid.txt');
cluster_average = zeros(1024,nocs);
cluster_frequency = zeros(nocs,1);
cluster_centroid = zeros(nocs,1);
x=importdata('x.txt');
normalized = 0; % set to 1 if spectra need to be normalized before cluster analysis

raylb4=100; % Data point before which rayleigh appears <<
raylcorrect=1; % set to 1 if rayleigh needs to be corrected <<
speclen=1024; % length of spectrum <<
xzeroI=28; %array index where x is zero <<
smoothFlag = 0; %set to 1 if smoothing is required
RamanBadDataRm = 0; %set to 1 if bad data at specific points need to be removed
BadData8 = 292;
noise_limit = 80; % noise limit to distinguish between noise and spectrum
repeat_smooth = 2;
noiselevel = 80;

x=importdata('x.txt');
for i=start_fileno:1:(start_fileno + nof-1)
   y_temp = importdata(sprintf('y%i.txt',i));
```

```
    if i==1
        A=y_temp;
    else
        A=vertcat(A,y_temp);
    end
end

A=reshape(A,[],nos);
yr=zeros(1024,1);
if raylcorrect == 1
    for i= 1:nos
        yr_temp = A(1:1024,i); % original spectrum

        y_max=max(yr_temp(raylb4:1024));
        y_min=min(yr_temp(raylb4:1024));

        [maxr,maxrI] = max(yr_temp(1:raylb4));   %to identify rayleigh and store its position to
maxrI
        %xr = x-x(maxrI);        %to change X-axis-so that the rayleigh is at zero

        if maxrI>xzeroI
            yr(1:(speclen-(maxrI-xzeroI))) = yr_temp((maxrI-xzeroI+1):speclen);
            yr((speclen-(maxrI-xzeroI)+1):speclen) = y_min;
        elseif maxrI<xzeroI
            yr(1:(xzeroI-maxrI)) = y_min;
            yr((xzeroI-maxrI+1):speclen) = yr_temp(1:(speclen-(xzeroI-maxrI)));
        end

        if RamanBadDataRm==1
            yr(BadData8) = (yr(BadData8-1)+yr(BadData8+1))/2;
        end

        for j= 1:repeat_smooth
            if smoothFlag==1
                yr = smooth(yr);          % to smoothen
            end
        end

        if (y_max-y_min)<noise_limit
            A(1:1024,i) = 0;
        else
            A(1:1024,i) = yr(1:1024); % normalized spectrum
        end

    end
end

C=zeros(nx,ny,1024);

Z=zeros(1024,1);
```

```
for i=1:1:nx
    for j=1:1:ny
    C(i,j,1:1024)=A(1:1024,(j+ny*(i-1)));
    if (max(C(i,j,200:1024))-min(C(i,j,200:1024)))<noiselevel
        C(i,j,1:1024) = Z(1:1024,1);
    end
    end
end
for i=1:1:nx
    for j=1:1:ny
    cluster_average(1:1024,(clusters(i,j)+1))                                    =
cluster_average(1:1024,(clusters(i,j)+1))+reshape(C(i,j,1:1024),1024,1);
    cluster_frequency((clusters(i,j)+1)) = cluster_frequency((clusters(i,j)+1)) + 1;
    cluster_centroid((clusters(i,j)+1)) = centroid((clusters(i,j)+1));
    dlmwrite(sprintf('%d.txt',11000000+(clusters(i,j)+1)*10000+((i-
1)*ny)+j),reshape(C(i,j,1:1024),1024,1),'delimiter','\t');
%          if(sum(reshape(C(i,j,1:1024),1024,1))~=0)
    if (max(C(i,j,200:1024))-min(C(i,j,200:1024)))>=noiselevel
        dlmwrite(sprintf('z%d.txt',11000000+((i-
1)*ny)+j),reshape(C(i,j,1:1024),1024,1),'delimiter','\t');
        end
    end
end

for i=1:1:nocs
    cluster_average(1:1024,i) = cluster_average(1:1024,i)/cluster_frequency(i);
end

dlmwrite('cluster_average.txt',cluster_average,'delimiter','\t');
dlmwrite('cluster_frequency.txt',cluster_frequency,'delimiter','\n');
dlmwrite('cluster_centroid.txt',cluster_centroid,'delimiter','\n');
clear all;
```

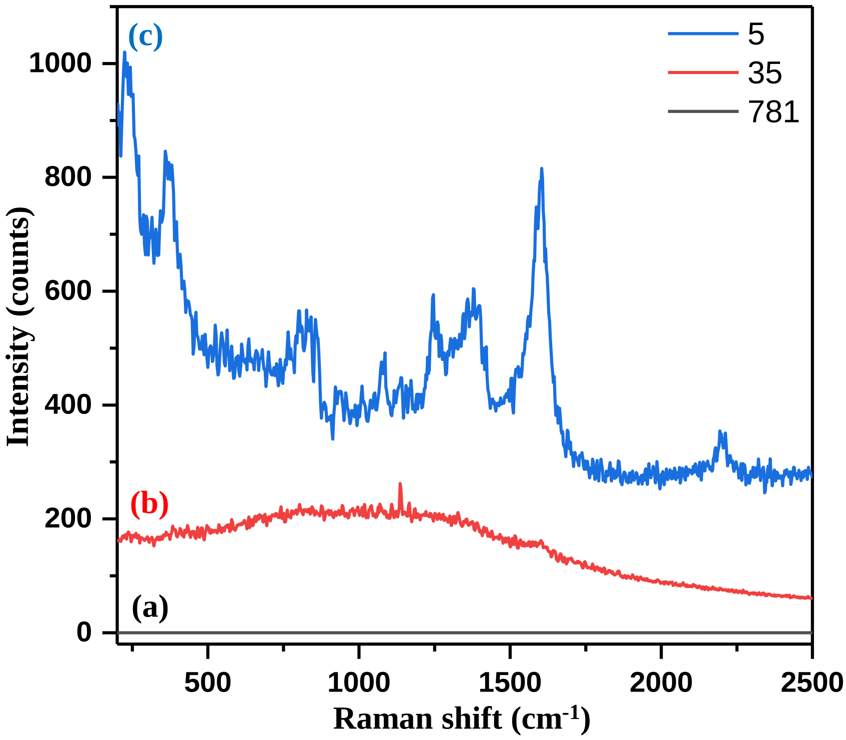

Figure S8. Set of three clusters out of 15 clusters which contain, (a) 781 spectra with no SERS features (blank spectrum), (b) 35 SERS spectra with broad background, and (c) 5 spectra with noisy SERS features.

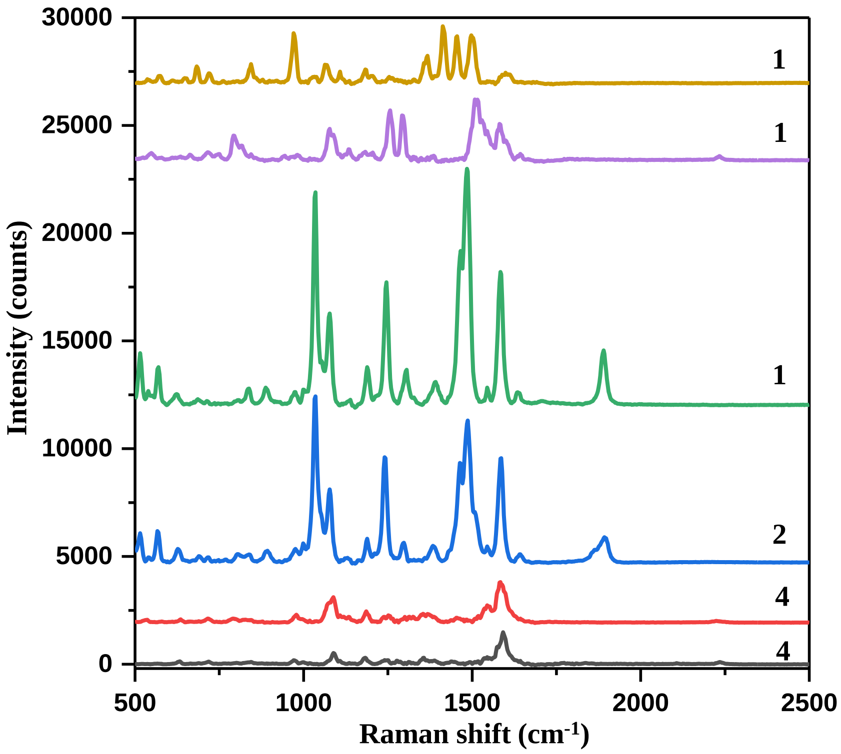

Figure S9. Set of 6 clusters as P-spectra out of 15 clusters which contain 4, 4, 2, 1, 1, and 1 spectra, respectively.

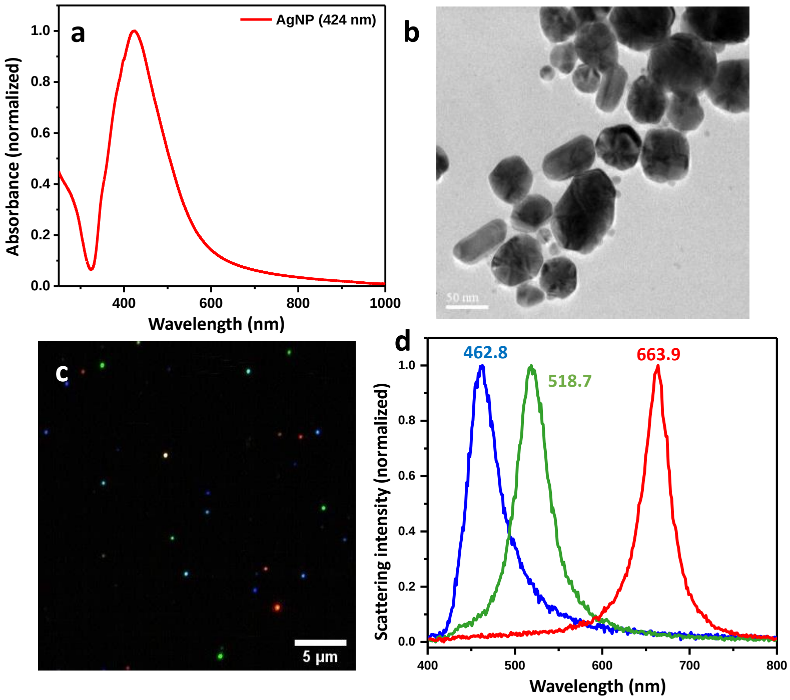

Figure S10. Spectroscopic and microscopic characterization of deuterated capped AgNPs, (a) UV-Vis absorption spectrum with maximum peak at 424 nm, (b) TEM image with polydispersed particles, (c) DF image, and (d) plasmonic scattering spectra of deuterated citrate-capped AgNPs.

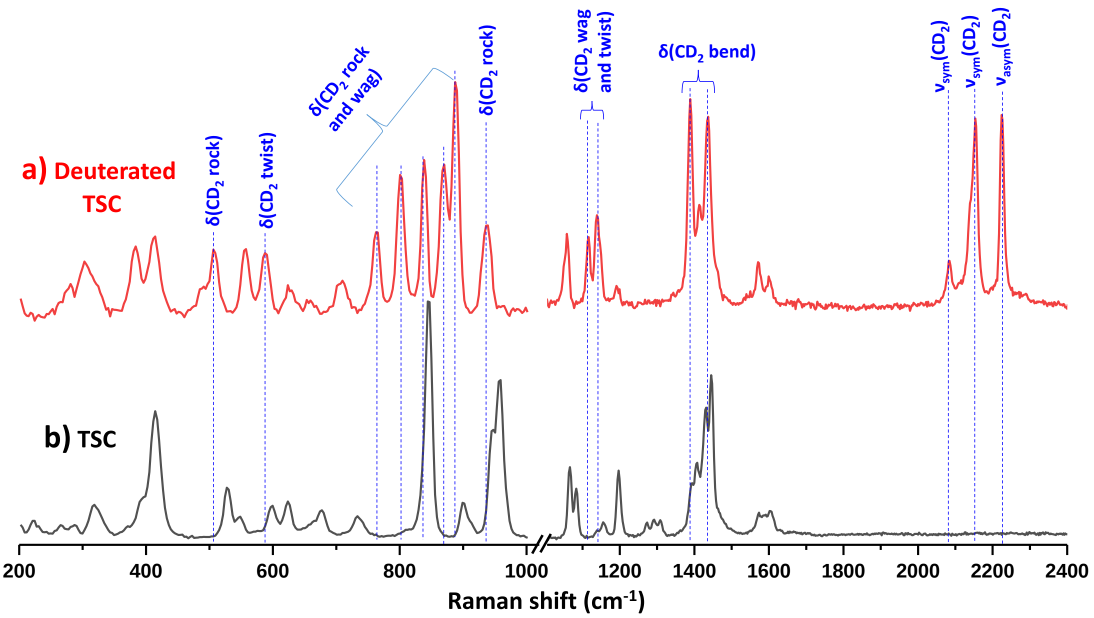

Figure S11. Comparison of Raman spectra of (a) deuterated TSC and (b) normal TSC, using bulk samples.

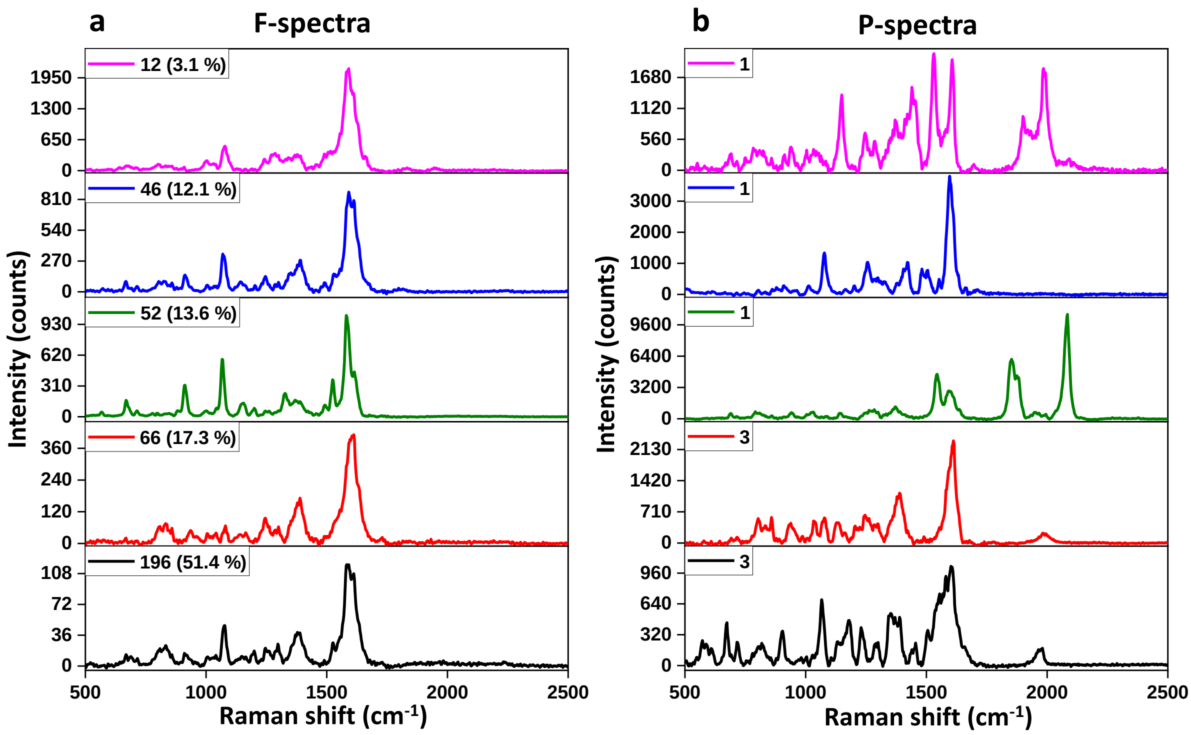

Figure S12. Cluster analysis of time-dependent SP-SERS spectra of deuterated citrate-capped AgNPs, (a) F-spectra and (b) P-spectra, with number of spectra observed.

References

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(3) Arthur, D.; Vassilvitskii, S. k-Means++: The Advantages of Careful Seeding. *Proc. eighteenth Annu. ACM-SIAM Symp. Discret. algorithms. Soc. Ind. Appl. Math. Philadelphia, PA, USA* **2007**, 1027–1035.

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III. APPENDICES

Appendix 1. Coordinates of sodium citrate, Ag_{55}, Ag_{25} and other Ag_{25}-citrate structures.

1. Sodium citrate ($Na_3C_6H_5O_7$)

O	-0.287728000	0.826372000	1.300655000
O	2.158453000	-0.299283000	1.331221000
O	1.390335000	-2.170024000	0.364647000
O	2.422009000	0.193671000	-1.816339000
O	-3.503193000	-1.237222000	-0.480474000
O	1.659781000	2.102369000	-0.890211000
O	-2.785993000	0.676975000	0.430821000
C	-0.075581000	-0.273624000	0.395296000
C	0.134736000	0.246952000	-1.074757000
C	-1.288466000	-1.221397000	0.471738000
C	1.236767000	-0.997866000	0.785593000
C	1.518058000	0.914131000	-1.298827000
C	-2.615813000	-0.559531000	0.104675000
H	-0.662549000	0.969092000	-1.280142000
H	0.036478000	-0.603240000	-1.755296000
H	-1.126982000	-2.094997000	-0.159341000
H	-1.378770000	-1.581702000	1.505820000
H	-1.220604000	1.099662000	1.115614000
Na	-4.744263000	0.568061000	-0.555540000
Na	1.666754000	1.895683000	1.279374000
Na	3.301592000	-1.298623000	-0.510336000

2. Silver 55 (Ag_{55})

Ag	15.345910000	13.509980000	15.901190000
Ag	16.057290000	12.267170000	13.652680000
Ag	17.686390000	12.061900000	16.084790000
Ag	17.490020000	14.576050000	14.633250000
Ag	15.088260000	10.770880000	15.951910000
Ag	14.773500000	14.853420000	13.648510000
Ag	13.275810000	12.487090000	14.478040000
Ag	17.396800000	14.548610000	17.532420000
Ag	15.896390000	12.168320000	18.353460000
Ag	15.570570000	16.267500000	16.054290000
Ag	13.150560000	12.488450000	17.384150000
Ag	12.964780000	14.976770000	15.949590000
Ag	14.611710000	14.772570000	18.369230000
Ag	16.797150000	11.011930000	11.343700000
Ag	20.015440000	10.617880000	16.129670000
Ag	19.630580000	15.625430000	13.280080000
Ag	14.856280000	8.046450000	15.890800000
Ag	14.220440000	16.164340000	11.308370000
Ag	11.245730000	11.458330000	12.957430000
Ag	19.447870000	15.567410000	19.039540000
Ag	15.835400000	18.982900000	16.093820000
Ag	11.061420000	11.369730000	18.742420000
Ag	10.662250000	16.464390000	15.829020000

Ag	13.963500000	15.997130000	20.725650000
Ag	18.481660000	10.775900000	13.663520000
Ag	18.283140000	13.325010000	12.170140000
Ag	15.806250000	9.417740000	13.547110000
Ag	15.496470000	13.587800000	11.166370000
Ag	13.988080000	11.222500000	12.004180000
Ag	19.982500000	13.168580000	14.759810000
Ag	17.486630000	9.202290000	16.115190000
Ag	19.856750000	13.057040000	17.672690000
Ag	18.360060000	10.663340000	18.498360000
Ag	16.963170000	15.998410000	12.184740000
Ag	19.661380000	15.673520000	16.174840000
Ag	17.783440000	17.404010000	14.623970000
Ag	12.931350000	9.641140000	14.425910000
Ag	15.635980000	9.316660000	18.369820000
Ag	12.891240000	9.625090000	17.345200000
Ag	12.617580000	13.862570000	12.064940000
Ag	15.056960000	17.698320000	13.604720000
Ag	12.321640000	16.342610000	13.499390000
Ag	11.024480000	11.384060000	15.841920000
Ag	10.821780000	13.970660000	14.376080000
Ag	18.052390000	13.154650000	19.941970000
Ag	17.769490000	17.391660000	17.547910000
Ag	16.733900000	15.769990000	20.026890000

Ag	13.719670000	10.996310000	19.785860000
Ag	15.216690000	13.420600000	20.833640000
Ag	13.202650000	17.833320000	15.831410000
Ag	14.948950000	17.595660000	18.488220000
Ag	10.490240000	13.944820000	17.139090000
Ag	12.427320000	13.676710000	19.902220000
Ag	12.280640000	16.307540000	18.403880000
Ag	16.462380000	10.825280000	20.679450000

3. Silver 25 (Ag_{25})

Ag	-0.526591000	4.548611000	0.471818000
Ag	-3.835957000	0.874027000	0.392892000
Ag	-1.148575000	1.792758000	0.619146000
Ag	1.616364000	2.736915000	0.830726000
Ag	-4.366444000	-1.924946000	0.522431000
Ag	-1.712819000	-0.977191000	0.891676000
Ag	1.011342000	-0.079974000	1.028763000
Ag	3.705683000	0.873098000	1.306293000
Ag	-2.286226000	-3.739358000	0.928996000
Ag	0.412379000	-2.860705000	1.219832000
Ag	3.145368000	-1.927431000	1.428854000
Ag	-4.036887000	2.170234000	-2.096629000
Ag	-1.331732000	3.091356000	-2.029127000
Ag	1.330521000	4.000458000	-1.825405000
Ag	-4.599037000	-0.588600000	-1.880428000

Ag	-1.905469000	0.299916000	-1.765493000
Ag	0.767176000	1.215954000	-1.563349000
Ag	3.441557000	2.125811000	-1.356325000
Ag	-2.520143000	-2.504653000	-1.545869000
Ag	0.187319000	-1.559923000	-1.374475000
Ag	2.883706000	-0.639169000	-1.168181000
Ag	5.598581000	0.267707000	-0.924594000
Ag	-0.362134000	-4.310377000	-1.033606000
Ag	2.290664000	-3.411458000	-0.823013000
Ag	4.940300000	-2.499723000	-0.627870000

4. $Ag_{25}C_5H_4O_5$ (SERS-F – 346 structure)

Ag	5.520465000	0.907704000	0.316855000
Ag	5.971178000	-1.761946000	-0.383074000
Ag	2.907973000	1.884224000	0.842834000
Ag	3.355290000	-0.890361000	0.194404000
Ag	3.837361000	-3.620691000	-0.600445000
Ag	0.274687000	2.824151000	1.277452000
Ag	0.733780000	0.099087000	0.584242000
Ag	1.205906000	-2.697449000	-0.148953000
Ag	-2.403508000	3.741646000	1.620845000
Ag	-1.916085000	0.995949000	1.073238000
Ag	-1.480586000	-1.730294000	0.284070000
Ag	-0.990844000	-4.484467000	-0.363638000
Ag	-4.547283000	1.977590000	1.343300000

Ag	-4.132137000	-0.772508000	0.707928000
Ag	-3.665436000	-3.536695000	-0.016903000
Ag	4.308579000	2.660354000	-1.450632000
Ag	1.685827000	3.615409000	-1.024903000
Ag	2.150798000	0.925782000	-1.873782000
Ag	-0.951144000	4.527045000	-0.589911000
Ag	-0.518348000	1.837986000	-1.389680000
Ag	-0.058537000	-0.864984000	-2.100695000
Ag	-3.191995000	2.804934000	-0.933292000
Ag	-2.708324000	0.074962000	-1.685327000
Ag	-2.247898000	-2.652225000	-2.400382000
Ag	-4.898316000	-1.752167000	-1.833280000
C	0.820034263	1.320037647	4.441468396
O	3.916001719	0.882275140	3.961329015
O	-2.141035803	0.028091868	5.556009558
O	3.458260994	2.916721939	3.119162173
O	-1.931426343	1.105601910	3.594223380
C	2.061305095	2.125424586	4.894728811
C	-0.400606402	1.701544548	5.332712191
C	3.241430806	1.968102698	3.933975732
C	-1.618814766	0.910610935	4.831893735
H	2.341230989	1.772666788	5.895277195
H	1.785746554	3.186195418	4.932803931
H	-0.571228731	2.781079491	5.212259890

H	-0.198296068	1.469397432	6.383789841
O	1.129787427	0.012181280	4.833341719

5. $Na_2Ag_{25}C_6H_5O_7$ (SERS-F – 43) structure

Ag	5.520465000	0.907704000	0.316855000
Ag	5.971178000	-1.761946000	-0.383074000
Ag	2.907973000	1.884224000	0.842834000
Ag	3.355290000	-0.890361000	0.194404000
Ag	3.837361000	-3.620691000	-0.600445000
Ag	0.274687000	2.824151000	1.277452000
Ag	0.733780000	0.099087000	0.584242000
Ag	1.205906000	-2.697449000	-0.148953000
Ag	-2.403508000	3.741646000	1.620845000
Ag	-1.916085000	0.995949000	1.073238000
Ag	-1.480586000	-1.730294000	0.284070000
Ag	-0.990844000	-4.484467000	-0.363638000
Ag	-4.547283000	1.977590000	1.343300000
Ag	-4.132137000	-0.772508000	0.707928000
Ag	-3.665436000	-3.536695000	-0.016903000
Ag	4.308579000	2.660354000	-1.450632000
Ag	1.685827000	3.615409000	-1.024903000
Ag	2.150798000	0.925782000	-1.873782000
Ag	-0.951144000	4.527045000	-0.589911000
Ag	-0.518348000	1.837986000	-1.389680000
Ag	-0.058537000	-0.864984000	-2.100695000

Ag	-3.191995000	2.804934000	-0.933292000
Ag	-2.708324000	0.074962000	-1.685327000
Ag	-2.247898000	-2.652225000	-2.400382000
Ag	-4.898316000	-1.752167000	-1.833280000
O	0.548763000	-0.126205000	2.608466000
H	-0.398563000	0.113621000	2.897185000
C	0.989926000	-1.011462000	3.635461000
O	-0.465435000	-2.699236000	2.630513000
O	1.219024000	-3.405418000	3.947542000
O	3.769708391	-2.950022451	3.643746733
O	-1.866029000	-1.546840000	5.434391000
O	4.753787596	-1.062855361	2.917156683
O	-1.702308000	0.013489000	3.824380000
C	2.525617000	-0.878251000	3.772406000
C	0.310154000	-0.582966000	4.971173000
C	0.550907000	-2.505084000	3.371353000
C	3.778940553	-1.688463100	3.435909329
C	-1.210931000	-0.694554000	4.786044000
H	2.862879000	-1.630545000	4.496425000
H	2.749967000	0.128945000	4.143677000
H	0.594986000	0.461209000	5.165049000
H	0.643987000	-1.221501000	5.796046000
Na	-2.598094000	-2.104913000	3.283721000
Na	4.297617388	-4.559615379	2.632164410

6. $NaAg_{25}C_6H_5O_7$ (SERS-T - 1) structure

Ag	2.496605000	3.098282000	-1.665644000
Ag	-0.365573000	2.728299000	-1.583074000
Ag	-3.207349000	2.348384000	-1.471175000
Ag	4.230888000	0.886525000	-1.931651000
Ag	1.384581000	0.446171000	-1.863032000
Ag	-1.477036000	0.085034000	-1.801691000
Ag	-4.280764000	-0.309596000	-1.729911000
Ag	3.118229000	-1.774673000	-2.115194000
Ag	0.307768000	-2.191538000	-2.053806000
Ag	-2.489366000	-2.563943000	-1.983306000
Ag	-0.549050000	4.136187000	0.974189000
Ag	-3.374752000	3.738309000	1.089532000
Ag	4.024894000	2.313972000	0.628912000
Ag	1.189164000	1.903657000	0.664823000
Ag	-1.627894000	1.483513000	0.744293000
Ag	-4.457279000	1.150946000	0.888501000
Ag	5.788924000	0.099405000	0.322923000
Ag	2.971875000	-0.322843000	0.470771000
Ag	0.149198000	-0.761766000	0.478106000
Ag	-2.695967000	-1.109572000	0.565216000
Ag	-5.483300000	-1.489795000	0.607721000
Ag	4.693459000	-2.530775000	0.138289000
Ag	1.913466000	-2.962630000	0.236633000

Ag	-0.916761000	-3.354716000	0.317915000
Ag	-3.693499000	-3.717346000	0.346520000
O	0.296192131	-1.817850222	3.249500827
H	1.127566786	-2.401094160	2.983144529
C	0.392978000	-1.040627000	4.128097000
O	2.505195198	0.050546815	3.041168770
O	1.189777578	1.229227172	2.750893918
O	-1.266028000	1.262706000	3.056655000
O	3.478139000	-1.986170000	5.215591000
O	-2.674679000	-0.533692000	2.881644000
O	2.442580000	-2.916165000	3.407776000
C	-1.003236000	-0.574535000	4.608968000
C	1.051844000	-2.010698000	5.158947000
C	1.503828320	0.236090182	3.714196880
C	-1.725008000	0.106219000	3.442145000
C	2.437014000	-2.372416000	4.601974000
H	-0.845569000	0.132215000	5.452798000
H	-1.604016000	-1.451103000	4.934083000
H	0.406094000	-2.914782000	5.248162000
H	1.161803000	-1.506669000	6.143791000
Na	4.052363000	-1.181211000	3.150619000

7. $Ag_{25}C_6H_5O_7$ (SERS-T - 1)

Ag	3.689200401	1.344305096	-1.177426490
Ag	4.606139649	-1.215548756	-1.830453751

Ag	1.065482529	1.773183811	-0.183682435
Ag	2.012904348	-0.884764732	-0.780823395
Ag	2.956245865	-3.505327242	-1.530248645
Ag	-1.586552017	2.153755017	0.726498345
Ag	-0.647583032	-0.457533333	0.080905058
Ag	0.312929101	-3.139056537	-0.603157229
Ag	-4.293181670	2.494555528	1.557434694
Ag	-3.295467553	-0.117527015	1.049598157
Ag	-2.396508769	-2.743724158	0.314881830
Ag	-1.413132949	-5.372550827	-0.290992854
Ag	-5.985555804	0.289230965	1.796410448
Ag	-5.072100886	-2.350731567	1.217376141
Ag	-4.122686475	-5.001238846	0.541104733
Ag	1.800399937	2.625420608	-2.744473345
Ag	-0.846704480	3.022184124	-1.845796424
Ag	0.060922486	0.432604894	-2.646533390
Ag	-3.495664493	3.374490808	-0.933214844
Ag	-2.609824989	0.782893422	-1.679467144
Ag	-1.678558512	-1.808367117	-2.343640974
Ag	-5.302624023	1.182918324	-0.741128099
Ag	-4.349920258	-1.433095099	-1.448991577
Ag	-3.413227310	-4.048123474	-2.116132947
Ag	-6.047935459	-3.698100944	-1.071038761
O	0.702747888	-0.125581656	2.292175192

H	-0.279630050	-0.038569798	2.686865347
C	0.417449049	-1.206658570	3.066434372
O	-0.769372897	-3.253744620	2.452048853
O	1.246207566	-3.455612133	3.435586057
O	3.092776035	-2.492591508	1.754637241
O	-2.556705888	-1.878933974	4.742869512
O	3.155528898	-0.459100841	0.943854564
O	-2.073434638	-0.381962864	3.352458348
C	1.879095832	-0.731210078	2.886480587
C	-0.083804062	-0.817646786	4.490246330
C	0.293741301	-2.777545092	2.964408274
C	2.775797643	-1.253932789	1.762567594
C	-1.573976170	-1.179340486	4.395436205
H	2.508681436	-1.323965658	3.561875449
H	1.929744158	0.329898200	3.158698940
H	-0.016707149	0.276577284	4.575041917
H	0.534913828	-1.291501312	5.259815655