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


# Supporting for "Elucidation of Charge-Transfer SERS Selection Rules by Considering the Excited State Properties and the Role of Electrode Potential"

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**Table S1.** Details of excited state energies, oscillator strength and type of transitions.* refers to selected CT state.

| BP86 | State number | Energy (eV) | Oscillator strength | Type of transition | $\Delta q^{cluster}_{s_0 \rightarrow s_n}$ |
|---|---|---|---|---|---|
| Py-$Ag_6$ | 1 | 1.64 | 0.0007 | CT | -0.76 |
| | 2 | 1.80 | 0.0020 | CT* | -0.74 |
| | 3 | 2.13 | 0.0000 | CT | -0.77 |
| | 4 | 2.31 | 0.0000 | CT | -0.80 |
| | 5 | 2.34 | 0.0119 | IC | +0.03 |
| | 6 | 2.47 | 0.0006 | IC | +0.02 |
| | 7 | 2.77 | 0.0006 | IC | +0.00 |
| | 8 | 3.03 | 0.0104 | IC+CT | -0.31 |
| | 9 | 3.10 | 0.0188 | CT | -0.02 |
| | 10 | 3.18 | 0.0000 | IC | |
| | 11 | 3.19 | 0.0123 | CT | |
| | 12 | 3.26 | 0.1174 | CT | |
| | 13 | 3.28 | 0.0011 | CT | |
| | 14 | 3.32 | 0.6527 | CT+IC | |
| | 15 | 3.34 | 0.0000 | IC | |
| | 16 | 3.40 | 0.0039 | CT | |
| | 17 | 3.42 | 0.0000 | CT | |
| | 18 | 3.44 | 0.0000 | CT | |
| | 19 | 3.45 | 0.8544 | IC+CT | |
| | 20 | 3.50 | 0.0000 | CT | |
| Py-$Ag_{20}$ | 1 | 1.65 | 0.0002 | CT | |
| | 2 | 1.67 | 0.0035 | CT | |
| | 3 | 1.69 | 0.0010 | CT+IC | |
| | 4 | 1.71 | 0.0046 | CT+IC | |
| | 5 | 1.73 | 0.0001 | CT+IC | |
| | 6 | 1.74 | 0.0002 | CT+IC | |
| | 7 | 1.75 | 0.0002 | CT+IC | |
| | 8 | 1.76 | 0.0004 | IC | |
| | 9 | 1.80 | 0.0001 | CT | |
| | 10 | 1.82 | 0.0003 | CT | |
| | 11 | 1.84 | 0.0053 | CT+IC | |
| | 12 | 1.87 | 0.0018 | CT+IC | |
| | 13 | 1.90 | 0.0018 | CT+IC | |
| | 14 | 1.91 | 0.0001 | CT+IC | |
| | 15 | 1.92 | 0.0046 | IC | |
| | 16 | 1.92 | 0.0047 | CT+IC | |
| | 17 | 1.96 | 0.0115 | IC | |
| | 18 | 1.99 | 0.0000 | IC | |
| | 19 | 2.03 | 0.0010 | CT+IC | |
| | 20 | 2.06 | 0.0002 | IC | |
| BHandHLYP | State number | Energy (eV) | Oscillator strength | Type of transition | |
| Py-$Ag_6$ | 1 | 2.67 | 0.0037 | IC | |

| | | | | |
|---|---|---|---|---|
| | 2 | 2.68 | 0.0396 | IC |
| | 3 | 3.04 | 0.0046 | IC |
| | 4 | 3.15 | 0.2211 | IC |
| | 5 | 3.17 | 0.0000 | IC |
| | 6 | 3.30 | 0.0594 | CT* |
| | 7 | 3.33 | 0.0000 | IC |
| | 8 | 3.54 | 1.4287 | IC+CT |
| | 9 | 3.72 | 1.6802 | IC+CT |
| | 10 | 3.85 | 0.0000 | CT |

**Table S2**. Magnitude of excited state gradients of $S_0 \rightarrow S_{CT1}$, $S_0 \rightarrow S_{IC}$ and $S_0 \rightarrow S_{IC+CT}$ transitions of Py-$Ag_6$ and $S_0 \rightarrow S_{CT1}$ transition of Py-$Ag_{20}$.

| Py-$Ag_6$ | Py-$Ag_{20}$ |
|---|---|
| $S_0 \rightarrow S_{CT1}$ | $S_0 \rightarrow S_{CT1}$ |
| $S_0 \rightarrow S_{CT2}$ | |
| $S_0 \rightarrow S_{IC}$ | |
| $S_0 \rightarrow S_{IC+CT}$ | |

$S_0 \rightarrow S_{CT1}$

| | | | | | |
|---|---|---|---|---|---|
| 1 | Ag | : | 0.000000010 | -0.001038126 | 0.005372618 |
| 2 | Ag | : | -0.000000003 | 0.008288789 | -0.006575878 |
| 3 | Ag | : | -0.000000009 | 0.000000104 | 0.003019725 |
| 4 | Ag | : | 0.000000034 | -0.000000054 | -0.021139899 |
| 5 | Ag | : | 0.000000002 | 0.001038128 | 0.005372591 |
| 6 | Ag | : | -0.000000018 | -0.008288773 | -0.006575880 |
| 7 | C | : | -0.034546041 | 0.000000019 | -0.033934891 |
| 8 | C | : | -0.015919198 | 0.000000188 | 0.032500184 |
| 9 | C | : | -0.000000041 | 0.000000011 | -0.039160754 |
| 10 | C | : | 0.015919208 | -0.000000065 | 0.032500194 |
| 11 | C | : | 0.034546028 | 0.000000098 | -0.033934927 |
| 12 | N | : | 0.000000018 | -0.000000033 | 0.064175446 |
| 13 | H | : | -0.000000038 | 0.000000002 | 0.000644164 |
| 14 | H | : | -0.001708642 | -0.000000001 | -0.002240211 |
| 15 | H | : | 0.001119383 | 0.000000027 | 0.001140038 |
| 16 | H | : | -0.001119385 | 0.000000028 | 0.001140054 |
| 17 | H | : | 0.001708656 | 0.000000001 | -0.002240199 |

$S_0 \rightarrow S_{CT1}$

| | | | | | |
|---|---|---|---|---|---|
| 1 | Ag | : | 0.001888819 | -0.000504461 | -0.000000103 |
| 2 | Ag | : | 0.006951272 | 0.010426942 | -0.000000567 |
| 3 | Ag | : | 0.005906932 | -0.005014766 | 0.013536162 |
| 4 | Ag | : | 0.005908978 | -0.005022673 | -0.013532376 |
| 5 | Ag | : | 0.003238070 | -0.005920361 | -0.000000398 |
| 6 | Ag | : | 0.001948532 | 0.002177444 | 0.007186505 |
| 7 | Ag | : | 0.001947725 | 0.002180026 | -0.007181835 |
| 8 | Ag | : | 0.007580336 | 0.012589477 | 0.000001512 |
| 9 | Ag | : | 0.009941622 | -0.007204620 | 0.008587170 |
| 10 | Ag | : | 0.009937878 | -0.007201212 | -0.008589827 |
| 11 | Ag | : | -0.007154148 | 0.001078740 | 0.000000174 |
| 12 | Ag | : | -0.007761119 | 0.004511116 | -0.012906218 |
| 13 | Ag | : | -0.007760492 | 0.004511533 | 0.012906814 |
| 14 | Ag | : | -0.009565492 | 0.007148398 | -0.008343259 |
| 15 | Ag | : | -0.009567217 | 0.007152345 | 0.008334840 |
| 16 | Ag | : | -0.007452054 | -0.010263383 | -0.000888474 |
| 17 | Ag | : | -0.007452758 | -0.010258389 | 0.000888385 |
| 18 | Ag | : | -0.004384693 | 0.012156911 | 0.000001160 |
| 19 | Ag | : | -0.005065807 | -0.006422134 | -0.013055357 |
| 20 | Ag | : | -0.005066500 | -0.006423162 | 0.013055603 |
| 21 | N | : | 0.027134271 | 0.000452193 | -0.000001162 |
| 22 | C | : | -0.014477785 | -0.000040009 | 0.000000784 |
| 23 | C | : | 0.012388464 | 0.000001599 | 0.005036591 |
| 24 | C | : | 0.012389450 | 0.000000863 | -0.005038053 |
| 25 | C | : | -0.011472125 | -0.000063279 | 0.011634754 |
| 26 | C | : | -0.011472020 | -0.000061953 | -0.011633241 |
| 27 | H | : | -0.000633362 | 0.000020029 | 0.000150018 |
| 28 | H | : | -0.000633304 | 0.000019797 | -0.000150047 |
| 29 | H | : | 0.000746968 | -0.000014702 | -0.000429934 |
| 30 | H | : | 0.000747017 | -0.000014819 | 0.000429951 |
| 31 | H | : | 0.001381648 | 0.000007424 | 0.000000059 |

$S_0 \rightarrow S_{CT2}$

| | | | | | |
|---|---|---|---|---|---|
| Ag | : | 0.000000013 | -0.001022314 | 0.005277610 |
| Ag | : | -0.000000001 | 0.008371974 | -0.006422384 |
| Ag | : | -0.000000001 | 0.000000092 | 0.003098701 |
| Ag | : | 0.000000025 | -0.000000058 | -0.018997390 |
| Ag | : | 0.000000005 | 0.001022303 | 0.005277551 |
| Ag | : | -0.000000010 | -0.008371967 | -0.006422403 |
| C | : | -0.010930489 | 0.000000298 | 0.051331204 |
| C | : | -0.005837519 | -0.000000007 | -0.050630729 |
| C | : | -0.000000207 | -0.000000064 | 0.008851400 |
| C | : | 0.005837526 | -0.000000016 | -0.050630715 |
| C | : | 0.010930478 | 0.000000231 | 0.051331149 |
| N | : | 0.000000047 | -0.000000192 | 0.011337616 |
| H | : | -0.000000012 | -0.000000021 | -0.001329347 |
| H | : | 0.000342615 | -0.000000004 | -0.000964243 |
| H | : | -0.000874033 | 0.000000009 | -0.000045279 |
| H | : | 0.000874023 | -0.000000031 | -0.000045294 |
| H | : | -0.000342618 | -0.000000009 | -0.000964212 |

$S_0 \rightarrow S_{IC}$

| | | | | | |
|---|---|---|---|---|---|
| 1 | Ag | : | 0.000000000 | -0.007572917 | -0.004272147 |
| 2 | Ag | : | 0.000000004 | -0.006750293 | 0.008114323 |
| 3 | Ag | : | 0.000000008 | 0.000001157 | -0.003315632 |
| 4 | Ag | : | 0.000000009 | 0.000000370 | -0.007825433 |
| 5 | Ag | : | -0.000000009 | 0.007570768 | -0.004271677 |
| 6 | Ag | : | -0.000000010 | 0.006751067 | 0.008113702 |
| 7 | C | : | -0.001695980 | 0.000000093 | 0.000189622 |
| 8 | C | : | 0.000349256 | -0.000000144 | 0.000358498 |
| 9 | C | : | -0.000000199 | 0.000000141 | -0.000162448 |
| 10 | C | : | -0.000349235 | -0.000000099 | 0.000358579 |
| 11 | C | : | 0.001695961 | 0.000000096 | 0.000189596 |
| 12 | N | : | 0.000000073 | -0.000000103 | 0.002081991 |
| 13 | H | : | -0.000000013 | -0.000000020 | -0.000290067 |
| 14 | H | : | -0.000760972 | 0.000000022 | 0.000126468 |
| 15 | H | : | 0.000247383 | -0.000000005 | 0.000034165 |
| 16 | H | : | -0.000247378 | -0.000000015 | 0.000034161 |
| 17 | H | : | 0.000760961 | 0.000000010 | 0.000126499 |

$S_0 \rightarrow S_{IC+CT}$

| | | | | | |
|---|---|---|---|---|---|
| 1 | Ag | : | 0.000000014 | 0.001560966 | 0.004855092 |
| 2 | Ag | : | -0.000000014 | 0.005294852 | -0.004508054 |
| 3 | Ag | : | 0.000000007 | 0.000000008 | 0.009461667 |
| 4 | Ag | : | 0.000000007 | -0.000000012 | -0.002873967 |
| 5 | Ag | : | 0.000000030 | -0.001560953 | 0.004855110 |
| 6 | Ag | : | -0.000000009 | -0.005294841 | -0.004508024 |
| 7 | C | : | 0.001907863 | -0.000000033 | -0.002082565 |
| 8 | C | : | -0.000300536 | 0.000000187 | 0.001232167 |
| 9 | C | : | -0.000000063 | -0.000000099 | -0.001239845 |
| 10 | C | : | 0.000300538 | -0.000000016 | 0.001232216 |
| 11 | C | : | -0.001907851 | 0.000000003 | -0.002082652 |
| 12 | N | : | 0.000000009 | -0.000000068 | -0.006265414 |
| 13 | H | : | -0.000000028 | 0.000000002 | -0.000671750 |
| 14 | H | : | -0.001458959 | -0.000000002 | 0.001759391 |
| 15 | H | : | 0.000725990 | 0.000000014 | -0.000649053 |
| 16 | H | : | -0.000725976 | 0.000000001 | -0.000649056 |
| 17 | H | : | 0.001458966 | -0.000000007 | 0.001759380 |

**Table S3**. Calculated dimensionless displacements of totally symmetric modes of Py adsorbed on silver electrode in different potentials.

| | | External electric field [a] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | +0.0030 | +0.0015 | 0.0000 | -0.0015 | -0.0030 | -0.0045 | -0.0060 | -0.0090 |
| BP86 | $\nu_{6a}$ | 0.9766 | 0.9446 | 0.9168 | 0.8899 | 0.8652 | 0.8409 | 0.8176 | 0.7744 |
| | $\nu_{9a}$ | 0.1606 | 0.8816 | 0.8753 | 0.8691 | 0.8636 | 0.8580 | 0.8527 | 0.8428 |
| | $\nu_{8a}$ | 0.9315 | 0.9255 | 0.9210 | 0.9161 | 0.9118 | 0.9070 | 0.9022 | 0.8928 |
| | | External electric field [a] | | | | | | | |
| | | | 0.0000 | -0.0005 | -0.0015 | -0.0030 | -0.0045 | -0.0060 | -0.0090 |
| BHandHLYP | $\nu_{6a}$ | | 0.9351 | 0.9311 | 0.9211 | 0.8931 | 0.8639 | 0.8303 | 0.7572 |
| | $\nu_{9a}$ | | 0.9019 | 0.9000 | 0.8930 | 0.8922 | 0.8808 | 0.8645 | 0.8238 |
| | $\nu_{8a}$ | | 0.8980 | 0.8984 | 0.8978 | 0.8909 | 0.8796 | 0.8634 | 0.8228 |

| Mode | Ref. 1 | | Ref. 2 | | | |
|---|---|---|---|---|---|---|
| | In -0.5 V | In -0.0 V | -0.25 V | -0.50 V | -0.75 V | -1.00 V |
| $\nu_{6a}$ | 0.0860 | 0.0000 | 0.0764 | 0.1107 | 0.2569 | 0.1996 |
| $\nu_{9a}$ | 0.1405 | 0.1167 | 0.0940 | 0.1550 | 0.4725 | 0.3818 |
| $\nu_{8a}$ | 0.1837 | 0.1499 | 0.1754 | -0.1777 | 0.3463 | 0.1956 |

[a]Direction and magnitude of applied external electric field in atomic unit.

**Table S4.** Bond length of Ag-N, and also C1-N and C1-C2 in pyridine before and after adsorption on the clusters and in the external electric field.

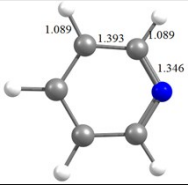
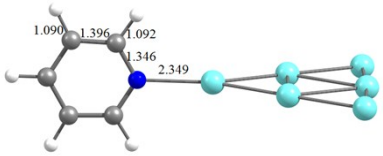
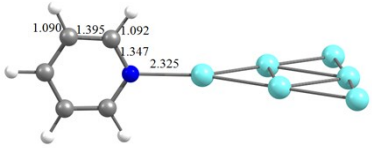
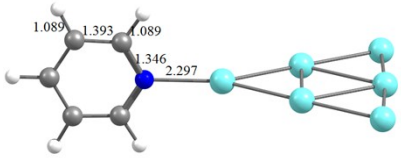
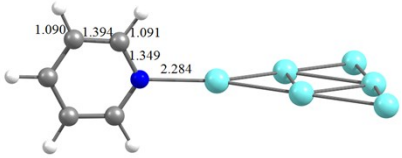
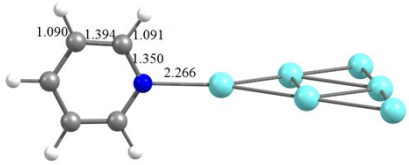
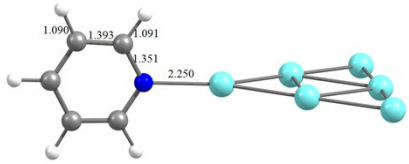
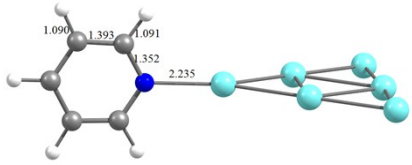
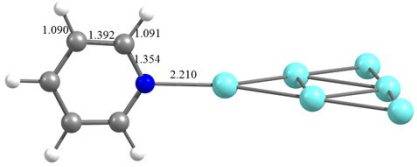
| | E field | |
|---|---|---|
| Py | 0.0000 |  |
| Py-$Ag_6$ | +0.0030 |  |
| | +0.0015 |  |
| | 0.0000 |  |
| | -0.0015 |  |
| | -0.0030 |  |
| | -0.0045 |  |
| | -0.0060 |  |
| | -0.0090 |  |

**Table S5.** Vibrational energy distribution analysis for $\nu_{6a}$, $\nu_{8a}$ and $\nu_{9a}$ modes of Py-$Ag_6$.

| Field | | VEDA |
|---|---|---|
| 0.0000 | $\nu_{6a}$ | 11% BEND CCN, 27% BEND CCC, 39% BEND CNC |
| | $\nu_{9a}$ | 24 STRE NC, 62% BEND HCC |
| | $\nu_{8a}$ | 42% STRE CC, 10% STRE NC |
| -0.0015 | $\nu_{6a}$ | 11% BEND CCN, 26% BEND CCC, 39% BEND CNC |
| | $\nu_{9a}$ | 24% STRE NC, 62% BEND HCC |
| | $\nu_{8a}$ | 42% STRE CC, 10% STRE NC |
| -0.0090 | $\nu_{6a}$ | 11% BEND CCN, 24% BEND CCC, 38% BEND CNC |
| | $\nu_{9a}$ | 21% STRE NC , 64% BEND HCC |
| | $\nu_{8a}$ | 43% STRE CC, 10% STRE NC |

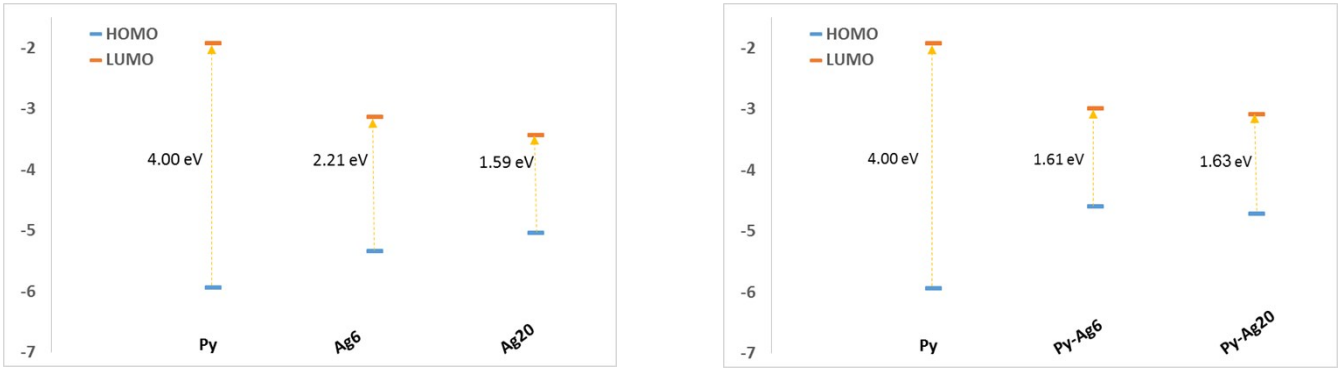



**Fig. S1.** Left panel: HOMO-LUMO gap of Py and Fermi level of pure clusters. It is apparent that Fermi level of selected cluster is between the HOMO-LUMO gap of Py. Numbers are the energy difference of Fermi level of metal cluster and LUMO energy of Py in eV. Right panel: HOMO-LUMO gap of Py and the combined systems.

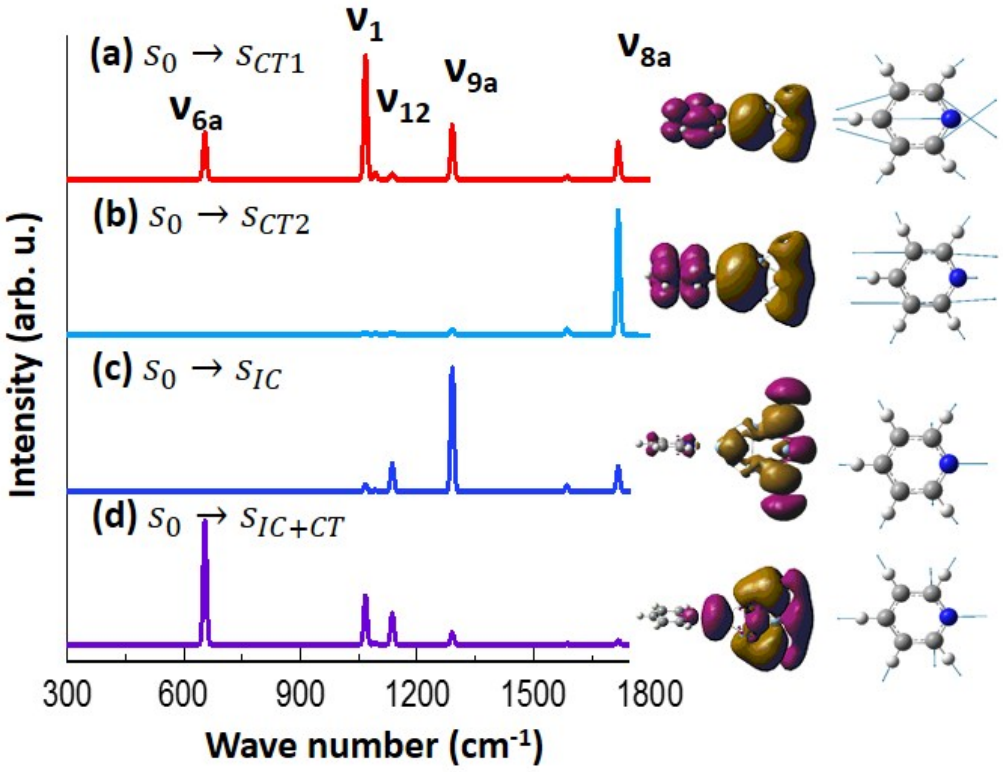



**Fig. S2**. SERS spectra for a) $^{S_0 \rightarrow S_{CT1}}$, b) $^{S_0 \rightarrow S_{CT2}}$, c) $^{S_0 \rightarrow S_{IC}}$ and d) $^{S_0 \rightarrow S_{IC+CT}}$ transitions of Py-$Ag_6$, by BHandHLYP level of theory.

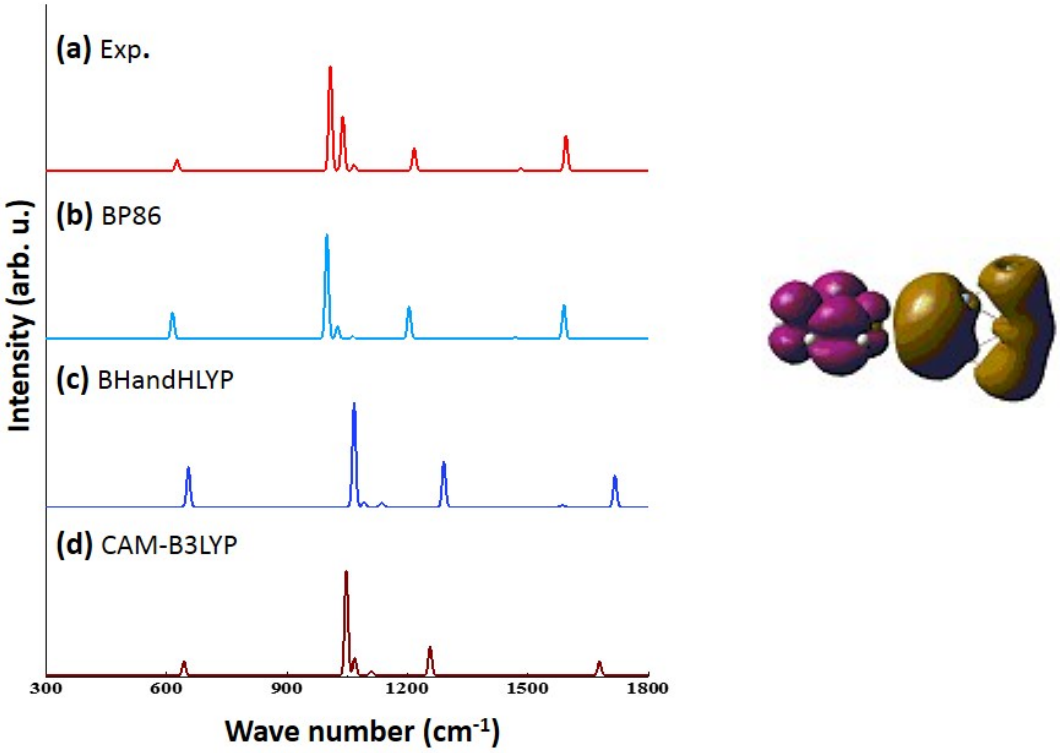



**Fig. S3** SERS spectra for $^{S_0 \rightarrow S_{CT1}}$ transition of Py-$Ag_6$ by BP86, BHandHLYP and CAM-B3LYP functionals in comparison to the experiment.

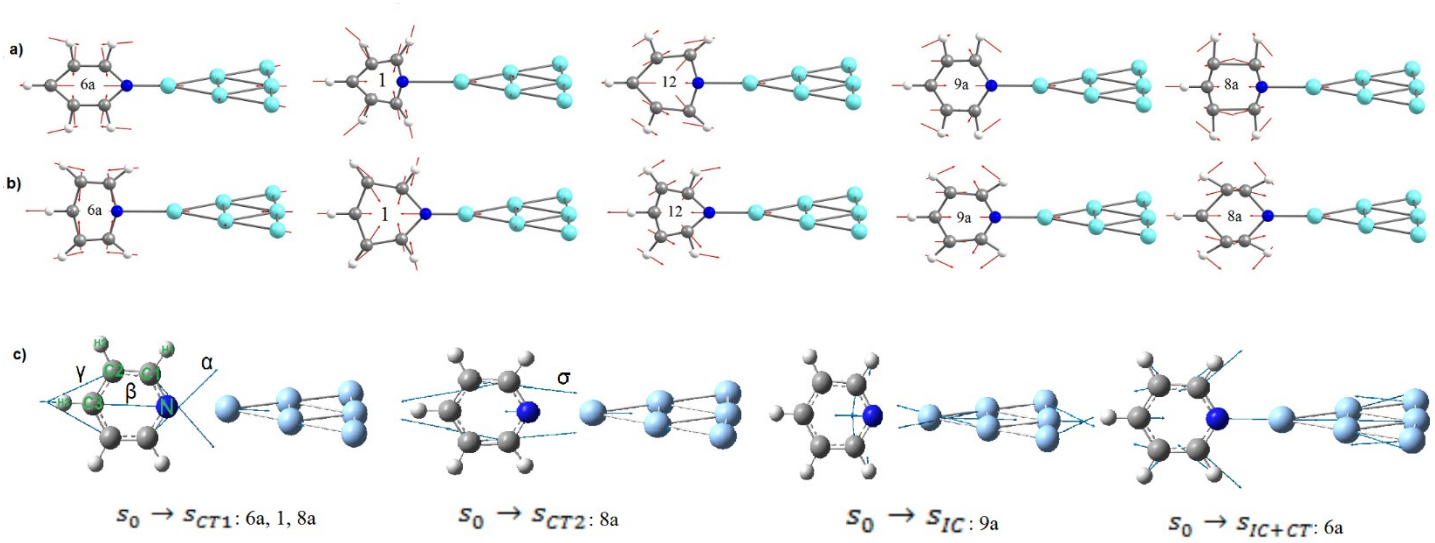



**Fig. S4.** Deformed structures of Py-$Ag_6$ upon totally symmetric normal modes in two compressed and extended frames displays in a and b part of the figure. c) Cartesian excited state gradient vectors of selected states of Py-$Ag_6$. Contribution of each vibrational normal mode in the gradient vectors have been shown under the gradient vectors.

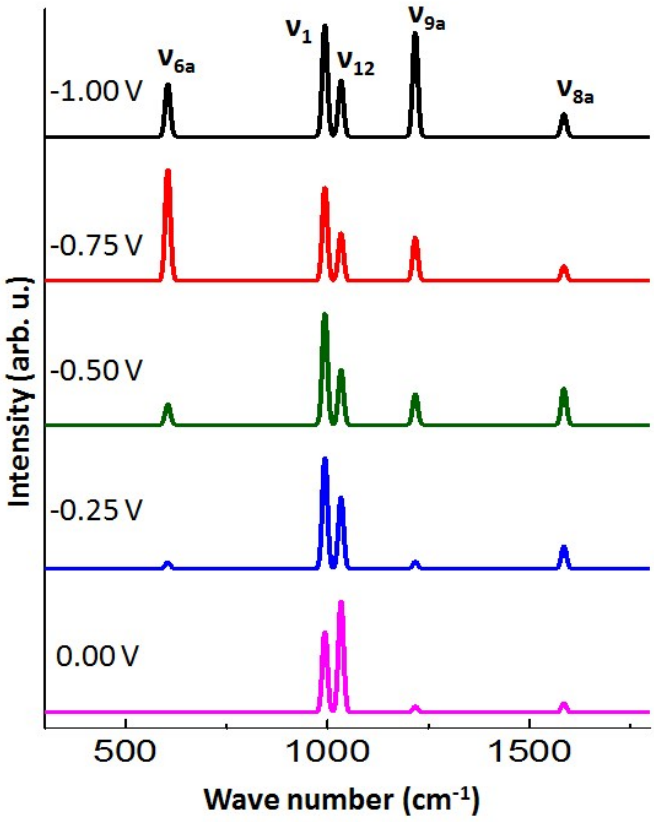



**Fig. S5** Fitting of the model parameters of eq. 3 based on experimental data from Ref. 2 was has been performed. In general, the experimental dimensionless displacements are determined along with finding a set of parameters i.e. homogeneous broadening, excitation energy and transition dipole moments by fitting of the experimental relative intensities and peaks position.

References

1. J. R. Lombardi and R. L. Birke, *J. Phys. Chem. C*, 2008, **112**, 5605.

2. J. F. Arenas, I. López Tocón, J. C. Otero and J. I. Marcos, *J. Phys Chem.*, 1996, **100**, 9254.