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

ELECTRONIC SUPPLEMENTARY INFORMATION

Comment on ‘‘Elucidation of charge-transfer SERS selection rules by considering the excited state properties and the role of electrode potential’’ by M. Mohammadpour, M. H. Khodabandeh, L. Visscher and Z. Jamshidi, *Phys. Chem. Chem. Phys.*, 2017, 19, 7833

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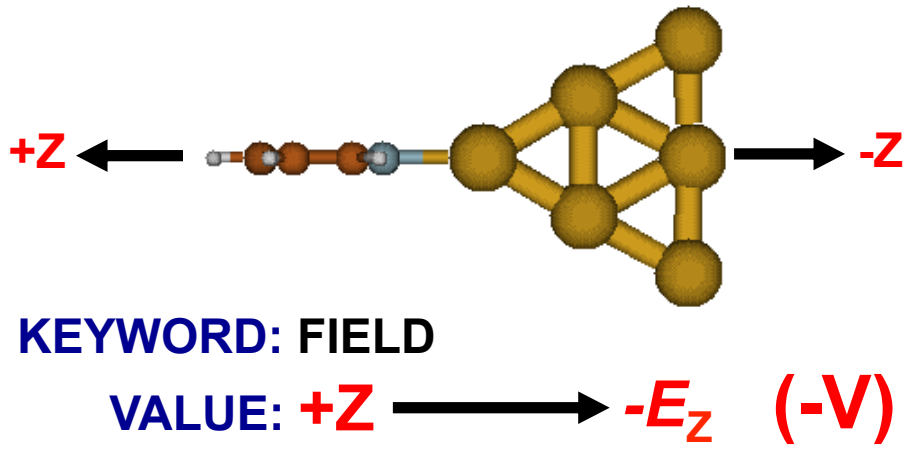


Figure S1. Py-Ag_6 perpendicular complex used in ref. 1 for modeling the pyridine bonded to the silver electrode, with the molecule pointing towards positive +z-axis. Gaussian 09 sign convention for finite fields: When a +Z valued is introduced in the FIELD keyword an electric field is applied in the opposite direction -E_z, i.e., pointing towards the metal, which corresponds to negative electrode potentials (-V).

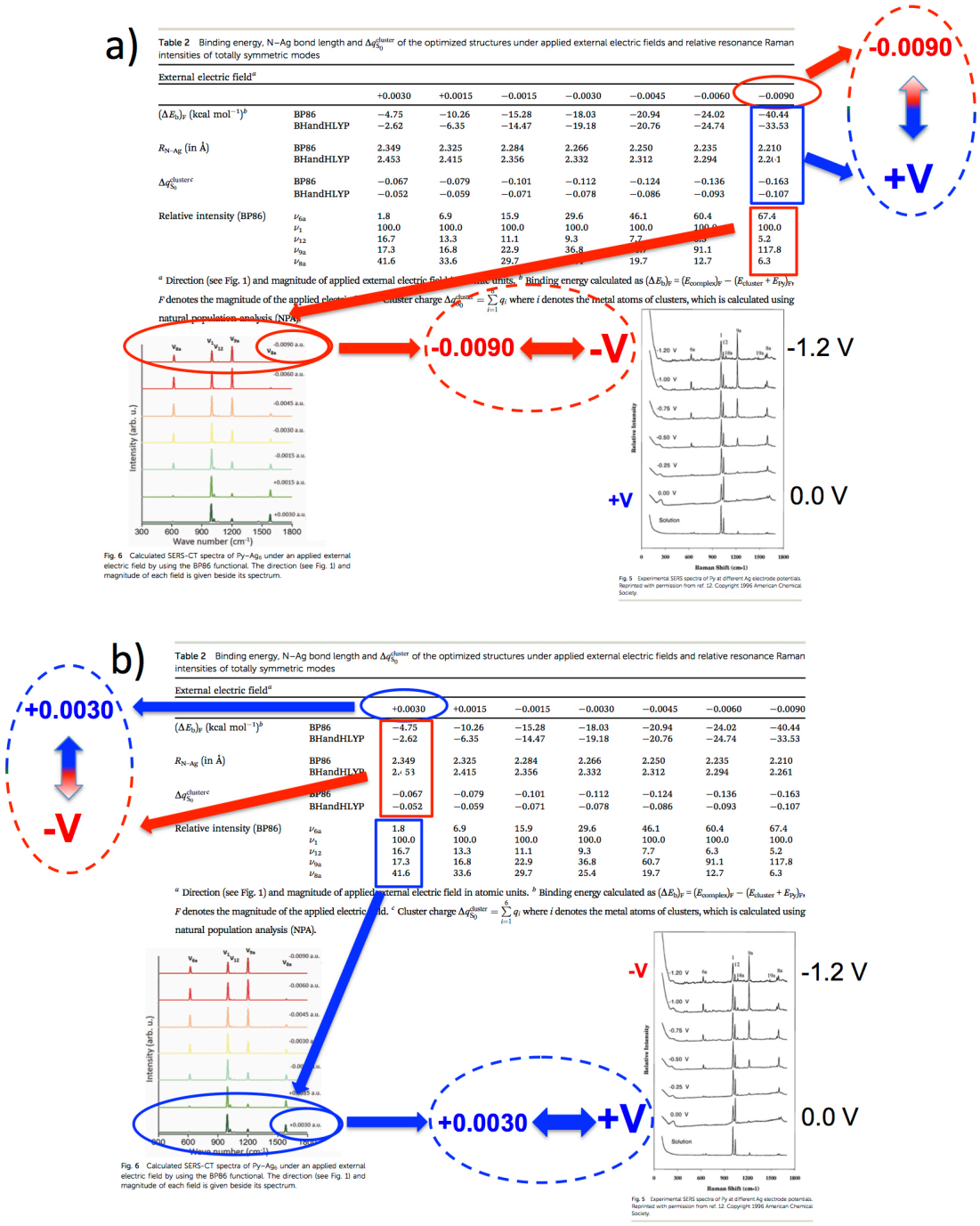


Figure S2. Schemes showing how set of results reported in Table 2 of ref. 1 corresponding to positive (+V) and negative (-V) electrode potentials are both labelled as a) negative (-0.0090 a.u.) or b) positive electric fields (+0.0030 a.u.).

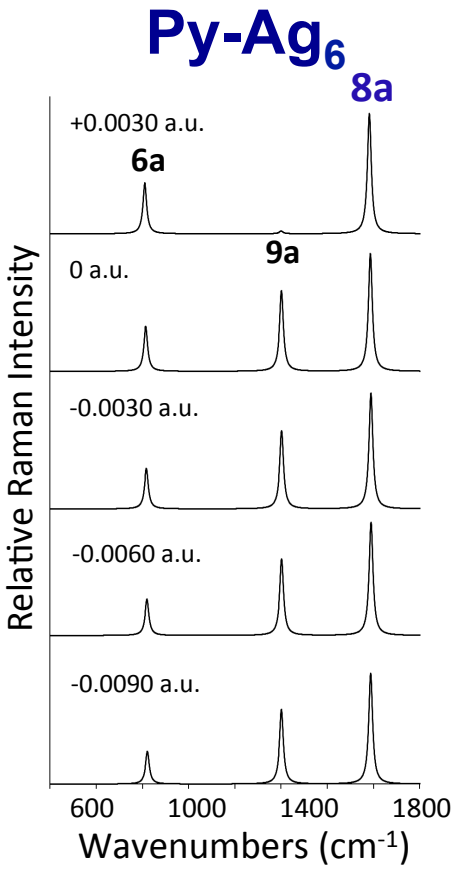
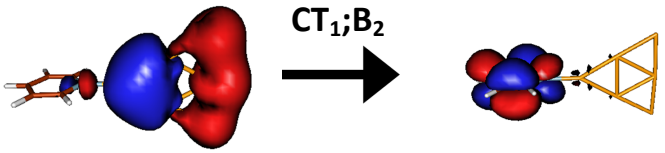


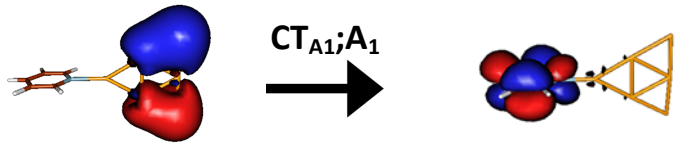
Figure S3. Effect of the electric field on the $I_{k,CT}^{preRR(1)}$ intensities of Py-Ag_6 calculated by using the dimensionless displacements $\Delta_{k,CTA1}$ reported in Table S3 of ref. 1 for the 6a, 9a and 8a modes. Electric fields labelled according to ref. 1. The value of $\Delta_{9a,CTA1}$=0.1606 for +0.0030 a.u. seems to be wrong.

Table S1 Dependence of the TD-BP86/Def2-TZVPP calculated properties of the $CT_1;B_2$ and $CT_{A1};A_1$ states of Py-Ag_6 under applied electric field (Gaussian 09 sign convention).



$HOMO_{Ag6};A_1$ $LUMO_{Py};B_2$

	Field (a.u.)[a]	Root[b]	Energy (eV)	Weight[c]	$\Delta q_{S0\rightarrow Sn}^{cluster}$[d]	f[e]
-V	0.009[f]	1	0.1382	0.71152	-0.134037	0.0001
	0.006	1	0.3990	0.70712	-0.712093	0.0001
	0.003	1	1.0065	0.70675	-0.759865	0.0002
	0.000	1	1.6424	0.70476	-0.736756	0.0006
	-0.003	2	2.2408	0.21700	-0.47096	0.0015
		3	2.4573	0.61045	-0.220648	0.0018
	-0.006	4	2.9467	0.47110	-0.339069	0.2511
		7	3.0574	-0.47958	-0.237323	0.3675
+V	-0.009	17	3.6195	0.69274	-0.474918	0.0137



$HOMO\text{-}1_{Ag6};B_2$ $LUMO_{Py};B_2$

	Field (a.u.)[a]	Root[b]	Energy (eV)	Weight[c]	$\Delta q_{S0\rightarrow Sn}^{cluster}$[d]	f[e]
-V	0.009[f]	2	0.2784	0.84796	0.056396	0.0163
	0.006	2	0.4103	0.70711	-0.666809	0.0036
	0.003	2	1.0874	0.70675	-0.779839	0.0018
	0.000	2	1.8005	0.70473	-0.761208	0.0017
	-0.003	4	2.4944	0.32150	-0.595706	0.0049
		5	2.7730	0.54816	-0.136401	0.0051
	-0.006	9	3.2480	0.40409	-0.179755	0.2871
		10	3.3704	0.55555	-0.358009	0.3661
+V	-0.009[g]	>20	-	-	-	-

[a]Applied electric field (Gaussian 09 sign convention). [b]Root showing the largest weight of the corresponding CT monoelectronic configuration. At -0.003 and -0.006 a.u. the CT configuration is mixed with intracluster excitations (IC) and is missing in the first 20 excited states calculated at -0.009 a.u. [c]Weight of the CT configuration. [d]Transferred Mulliken´s charges (a.u.) from Py to Ag_6 in the $S_0 \rightarrow S_{CT}$ transition. [e]Oscillator strength. [f]CT states are too close to the ground electronic state at this particular field. This is why the corresponding $\Delta q_{S0\rightarrow Sn}^{cluster}$ deviated from the remaining ones. [g]CT_{A1} state does not appear in the first twenty excited states calculated at this field.

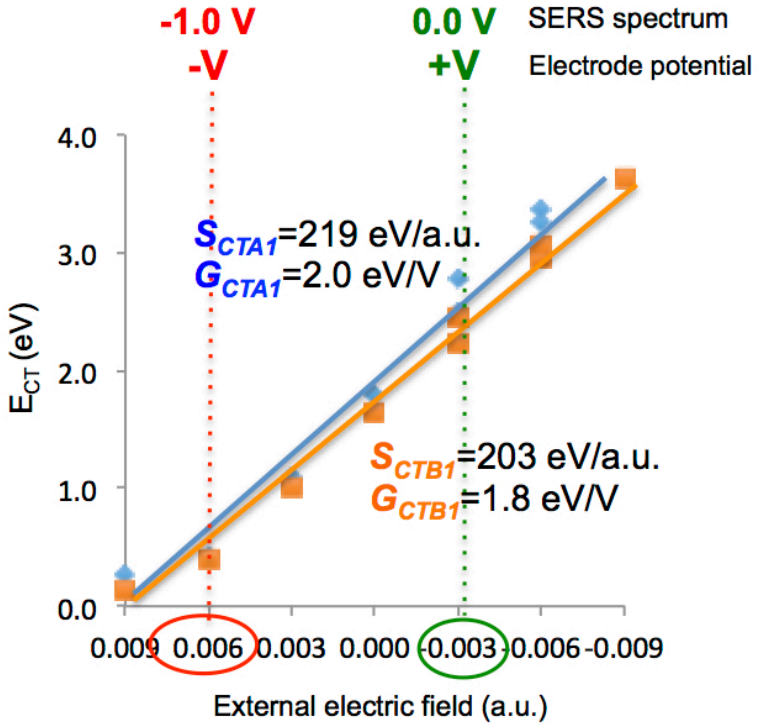


Figure S4. Dependence of the TD-BP86/Def-2TZVPP calculated energies of the $CT_1;B_2$ (orange) and $CT_{A1};A_1$ (blue) states of Py-Ag_6 under applied electric field (Gaussian 09 sign convention).