Supporting Information

Investigation of the Charge-transfer Surface-Enhanced Resonance Raman Spectra of Benzene-like Derivatives Compounds under the Effect of External Electric Field

Sahar Ashtari-Jafari[a], Mohammad Hassan Khodabandeh[a] and Zahra Jamshidi [a,b†]

[a] *Chemistry & Chemical Engineering Research Center of Iran (CCERCI), Pajohesh Blvd, 17th Km of Tehran-Karaj Highway, P. O. Box 1496813151 Tehran, Iran.*

[b] *Chemistry Department, Sharif University of Technology, Tehran 11155-9516, Iran.*

† *Correspondence to:* njamshidi@sharif.edu, na.jamshidi@gmail.com

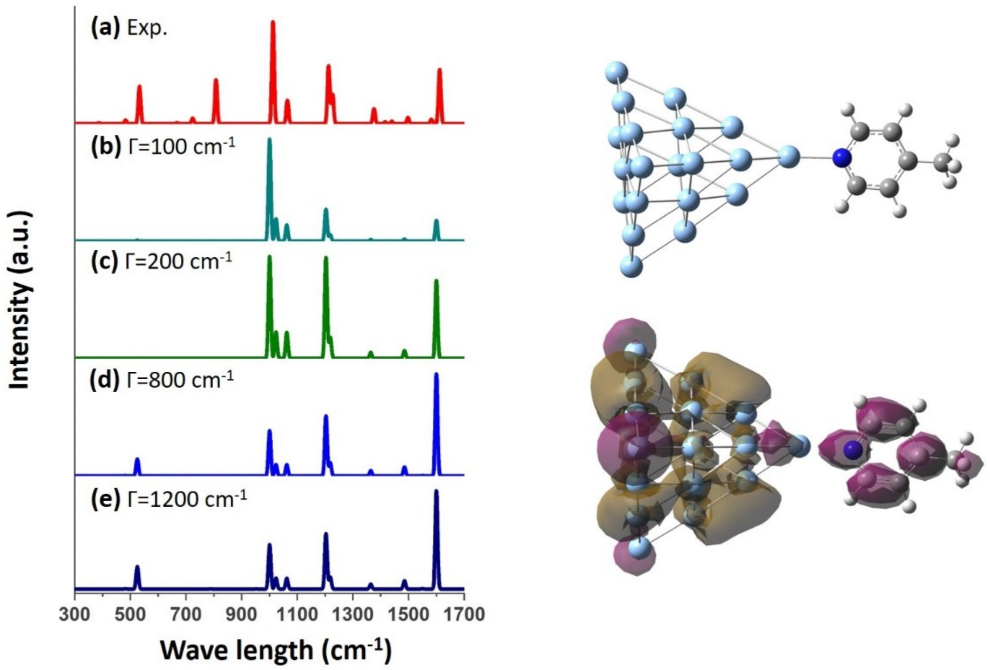


Fig. S1 The experimental (a) and computational (b-e) SERS spectra of 4MPy-Ag_{20}. The experimental spectra is a result of fitting with experimental data which gave Γ= 100 cm^{-1}, the computational spectra are calculated using Γ= 100, 200, 800 and 1200 cm^{-1}.

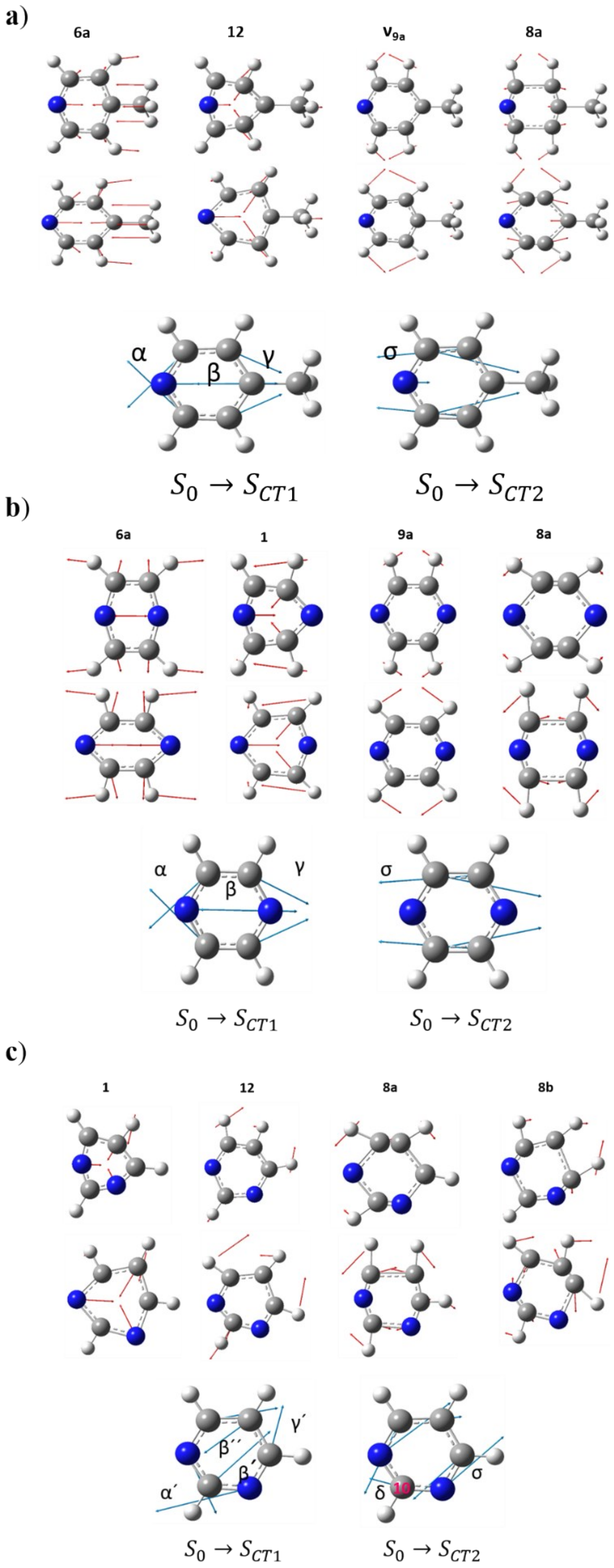
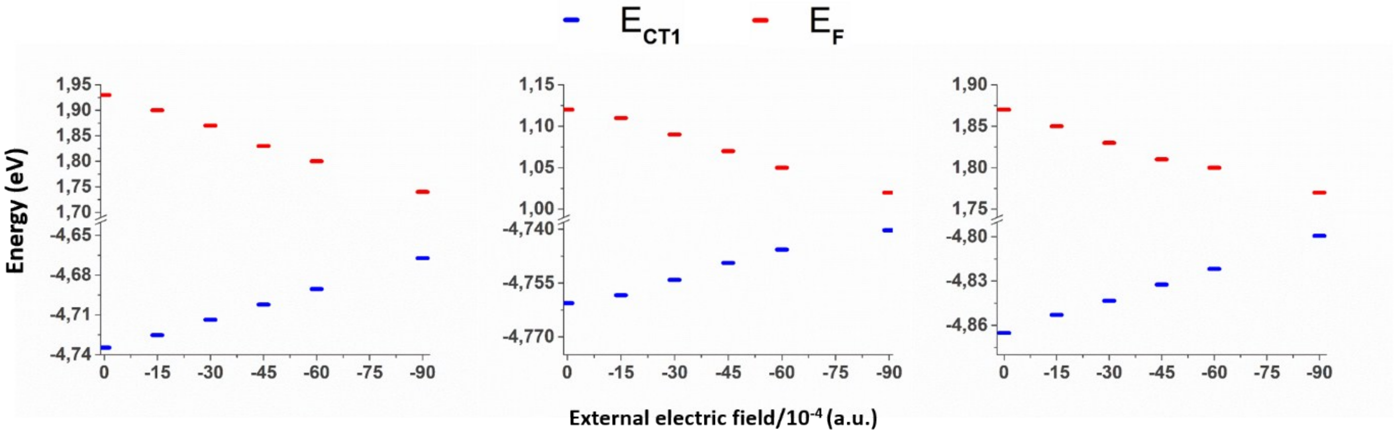


Fig. S2 The vibrational displacements of the dominant vibrational modes in two compact and decentered forms alongside the excited-state gradients for CT1 and CT2 transitions of a) 4MPy–Ag_6, b) Pyrazine–Ag_6 and c) Pyrimidine–Ag_6.



a) b) c)

Fig. S3 The CT transition and the Fermi level Energy against the applied electric field for a) 4MPy–Ag_6, b) Pyrazine–Ag_6 and c) Pyrimidine–Ag_6

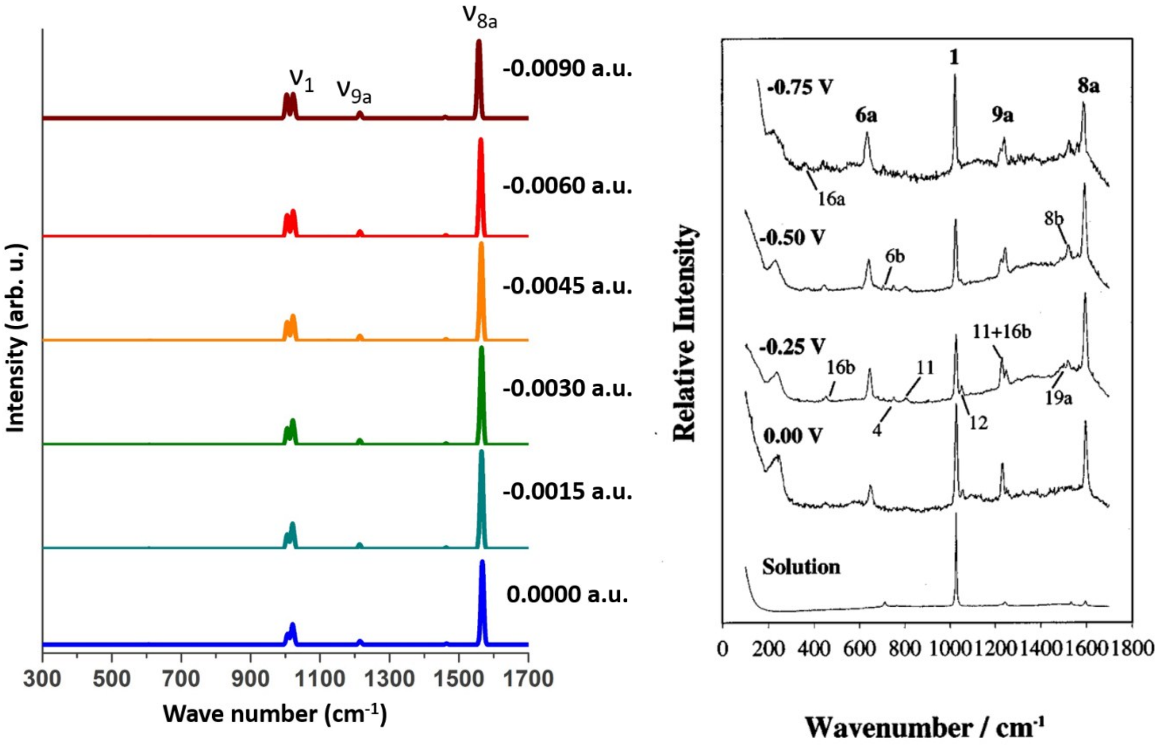


Fig. S4 The calculated SERS-CT2 spectra of Pyrazine – Ag$_6$ in the presence of various external electric fields with values written beside each spectrum (right) and the experimental SERS spectra of Pyrazine at various Ag electrode potentials (right) reprinted with permission from ref. 1. Copyright 2002 American Institute of Physics. The direction of the external electric field in the calculated spectra is displayed in Fig. 1 (of main article).

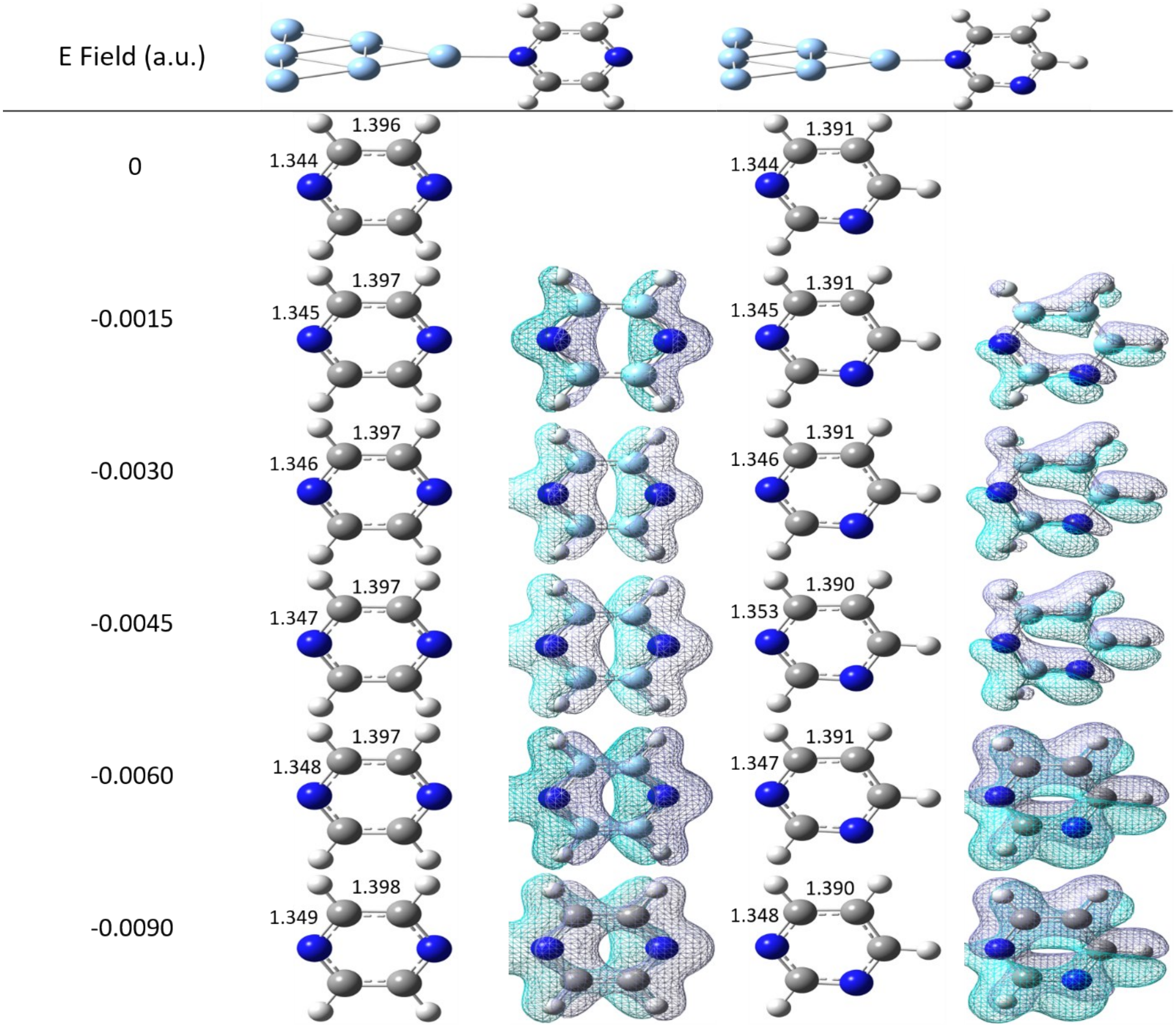
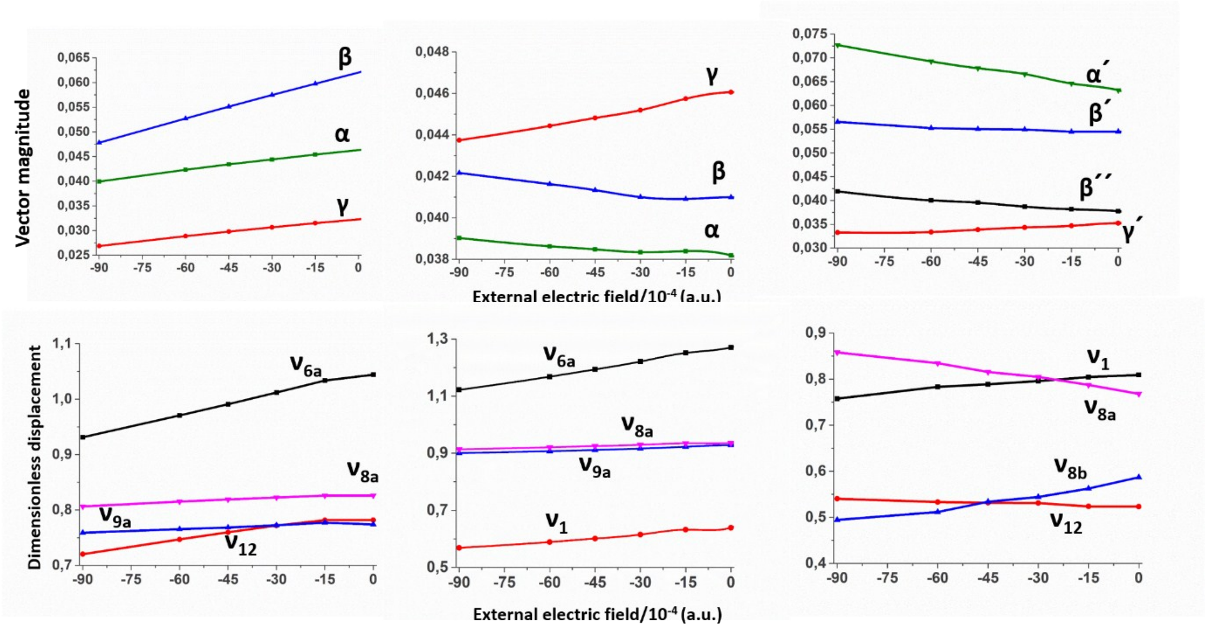


Fig. S5 The variation of C – C and C – N bond lengths and $\Delta\rho_{\ Field}$ with different amounts of external electric field for Pyrazine–Ag_6 and Pyrimidine–Ag_6.



a) b) c)

Fig. S6 The variation of excited-state vector gradient magnitude and the dimensionless displacements of the dominant vibrational modes with different applied electric fields for a) 4MPy–Ag_6, b) Pyrazine–Ag_6 and c) Pyrimidine–Ag_6.

Table S1. The cartesian gradient vectors of the CT1 transition for Ag_6-4MPy, Ag_6-Pyrazine and Ag_6-Pyrimidine.

		Cartesian Gradient Vector		
		X	Y	Z
Ag_6-4MPy	C :	0.020041957	-0.035626351	-0.022083780
	C :	0.008610750	0.027060506	-0.015298446
	C :	-0.003835370	-0.030373889	0.001713171
	C :	-0.007993977	0.030485382	0.007055842
	C :	-0.019894040	-0.027413225	0.031692338
	N :	0.000256598	0.061569872	-0.009100674
	H :	0.000445956	-0.002802415	-0.000412943
	H :	0.000590299	0.000953975	-0.000958554
	H :	-0.000659487	-0.002581445	0.001086735
	H :	-0.000595825	0.001199635	0.000625426
	C :	0.002824217	0.007007253	0.001042810
	H :	-0.001441685	-0.001864012	0.000313215
	H :	0.002017091	-0.005488773	0.002341169
	H :	-0.000398197	-0.002064802	-0.001079957
	Ag :	0.000057227	-0.021085675	0.003236540
	Ag :	-0.006381698	-0.006920491	-0.003776536
	Ag :	0.006356796	-0.005665176	0.005573922
	Ag :	0.001324121	0.005670124	0.000179554
	Ag :	-0.001421405	0.005355639	-0.001841007
	Ag :	0.000094999	0.002642149	-0.000315819
		X	Y	Z
Ag_6-Pyrazine	Ag :	0.000208909	0.001584924	0.000000449
	Ag :	0.003678287	0.003125602	0.000000187
	Ag :	-0.004701528	-0.000011369	-0.000000851
	Ag :	-0.025104570	0.000006212	0.000000195
	Ag :	0.000217803	-0.001577143	0.000000407
	Ag :	0.003681058	-0.003130016	0.000000200
	C :	-0.034123070	0.000000492	-0.030940525
	C :	0.034777275	-0.000003004	-0.015770368
	C :	-0.034125852	0.000000639	0.030930565
	N :	0.064545257	0.000003056	0.000006335
	H :	-0.003182784	0.000000690	-0.000807822
	H :	0.001755660	0.000000029	-0.001410713
	H :	-0.003182673	0.000000699	0.000807204
	C :	0.034771388	-0.000003001	0.015776854
	H :	0.001755650	-0.000000005	0.001411030
	N :	-0.040990919	0.000002406	-0.000002790

		X	Y	Z
Ag$_6$-Pyrimidine	Ag :	0.000000958	0.000213179	-0.001566446
	Ag :	-0.000113556	0.003778436	-0.003223612
	Ag :	0.000012931	-0.004768074	0.000000045
	Ag :	0.000265443	-0.025958428	-0.000000018
	Ag :	0.000000966	0.000213200	0.001566411
	Ag :	-0.000113587	0.003778372	0.003223584
	C :	0.058754508	-0.027541521	-0.000000346
	C :	-0.002810985	0.015552928	-0.000000195
	C :	0.035769576	-0.037871421	-0.000000368
	C :	-0.007214671	-0.025730308	0.000000303
	N :	-0.042182880	0.054276932	0.000000262
	H :	0.001103568	0.001166275	-0.000000073
	H :	-0.000248435	-0.004248356	0.000000089
	H :	0.000586283	0.000925995	0.000000146
	H :	-0.001398434	-0.000909619	-0.000000111
	N :	-0.042393473	0.047079569	0.000000101

Table S2. The power two of the dimensionless displacements (Δ^2) along the most intense vibrational normal modes of Ag_6-4MPy, Ag_6-Pyrazine and Ag_6-Pyrimidine for the CT1 transition state.

	ν_{6a}	**ν_{1}**	**ν_{12}**	**ν_{9a}**	**$\nu_{9a'}$**	**ν_{8a}**
Ag_6-4MPy	1.090	0.005	0.608	0.599	0.111	0.682
	ν_{6a}	**ν_{12}**	**ν_{1}**	**ν_{9a}**	**ν_{8a}**	
Ag_6-Pyrazine	1.614	0.123	0.408	0.862	0.875	
	ν_{6a}	**ν_{1}**	**ν_{12}**	**ν_{19a}**	**ν_{8b}**	**ν_{8a}**
Ag_6-Pyrimidine	0.222	0.695	0.191	0.491	0.392	0.741

Table S3. The relative intensities of the main vibrational modes in the SERS spectra corresponding to CT1 transition of 4MPy–Ag_6 under the effect of field (in a.u.).

Field	ν_{6a}	ν_{1}	ν_{12}	ν_{9a}	$\nu_{9a'}$	ν_{8a}
0	0.027	0.001	0.093	0.027	0.007	0.026
-0.0015	0.029	0.002	0.093	0.032	0.007	0.023
-0.0030	0.037	0.003	0.093	0.050	0.012	0.017
-0.0045	0.050	0.004	0.093	0.078	0.017	0.010
-0.0060	0.053	0.005	0.077	0.093	0.018	0.005
-0.0090	0.042	0.005	0.048	0.093	0.015	0.008

Table S4. The relative intensities of the main vibrational modes in the SERS spectra corresponding to CT1 transition of Pyrazine-Ag6 under the effect of field (in a.u.).

Field	**ν_{6a}**	**ν_{12}**	**ν_{1}**	**ν_{9a}**	**ν_{8a}**
0	0.013	0.010	0.033	0.011	0.093
-0.0015	0.011	0.012	0.038	0.010	0.093
-0.0030	0.010	0.018	0.044	0.009	0.093
-0.0045	0.015	0.022	0.044	0.011	0.093
-0.0060	0.026	0.024	0.043	0.01	0.093
-0.0090	0.077	0.028	0.040	0.047	0.093

Table S5. The relative intensities of the main vibrational modes in the SERS spectra corresponding to CT2 transition of Pyrazine–Ag_6 under the effect of field (in a.u.).

Field	ν_{6a}	ν_{12}	ν_{1}	ν_{9a}	ν_{8a}
0	0.000	0.012	0.023	0.004	0.093
-0.0015	0.000	0.014	0.024	0.004	0.093
-0.0030	0.000	0.016	0.023	0.004	0.093
-0.0045	0.000	0.018	0.024	0.005	0.093
-0.0060	0.000	0.021	0.025	0.005	0.093
-0.0090	0.000	0.028	0.029	0.006	0.093

Table S6. The relative intensities of the main vibrational modes in the SERS spectra corresponding to CT2 transition of Pyrimidine–Ag_6 under the effect of field.

Field	**ν_{6a}**	**ν_1**	**ν_{12}**	**ν_{19a}**	**ν_{8b}**	**ν_{8a}**
0	0.008	0.093	0.036	0.015	0.018	0.060
-0.0015	0.008	0.093	0.037	0.016	0.018	0.071
-0.0030	0.007	0.093	0.039	0.018	0.021	0.090
-0.0045	0.005	0.082	0.035	0.018	0.021	0.093
-0.0060	0.004	0.074	0.032	0.017	0.019	0.093
-0.0090	0.002	0.058	0.029	0.017	0.019	0.093

Table S7. The relative intensities of the main vibrational modes in the SERS spectra corresponding to CT1 transition of Pyrimidine–Ag_6 under the effect of field.

Field	**ν_{6a}**	**ν_1**	**ν_{12}**	**ν_{19a}**	**ν_{8b}**	**ν_{8a}**
0	0.019	0.093	0.039	0.035	0.020	0.034
-0.0015	0.015	0.093	0.036	0.030	0.014	0.026
-0.0030	0.010	0.093	0.032	0.024	0.009	0.018
-0.0045	0.007	0.093	0.028	0.019	0.006	0.012
-0.0060	0.005	0.093	0.026	0.016	0.004	0.008
-0.0090	0.003	0.093	0.026	0.013	0.003	0.005

References

1. J. F. Arenas, M. S. Woolley, I. L. Tocón, J. C. Otero and J. I. Marcos, *The Journal of Chemical Physics*, 2000, **112**, 7669-7683.
2. S. P. Centeno, I. López-Tocón, J. F. Arenas, J. Soto and J. C. Otero, *The Journal of Physical Chemistry B*, 2006, **110**, 14916-14922.