Modelling the Effect of the Electrode Potential on the Metal-Adsorbate Surfaces States: Relevant States in the Charge Transfer Mechanism of SERS

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Supplementary Material (ESI) for Chemical Communications

Electronic Supporting Information

Index

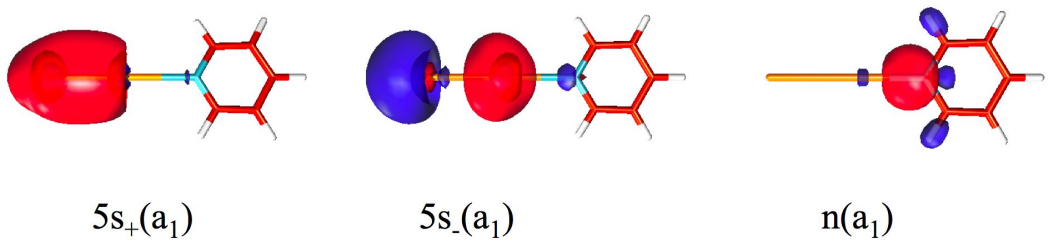

Figure.S1. Active space for Ag_2Py cluster.

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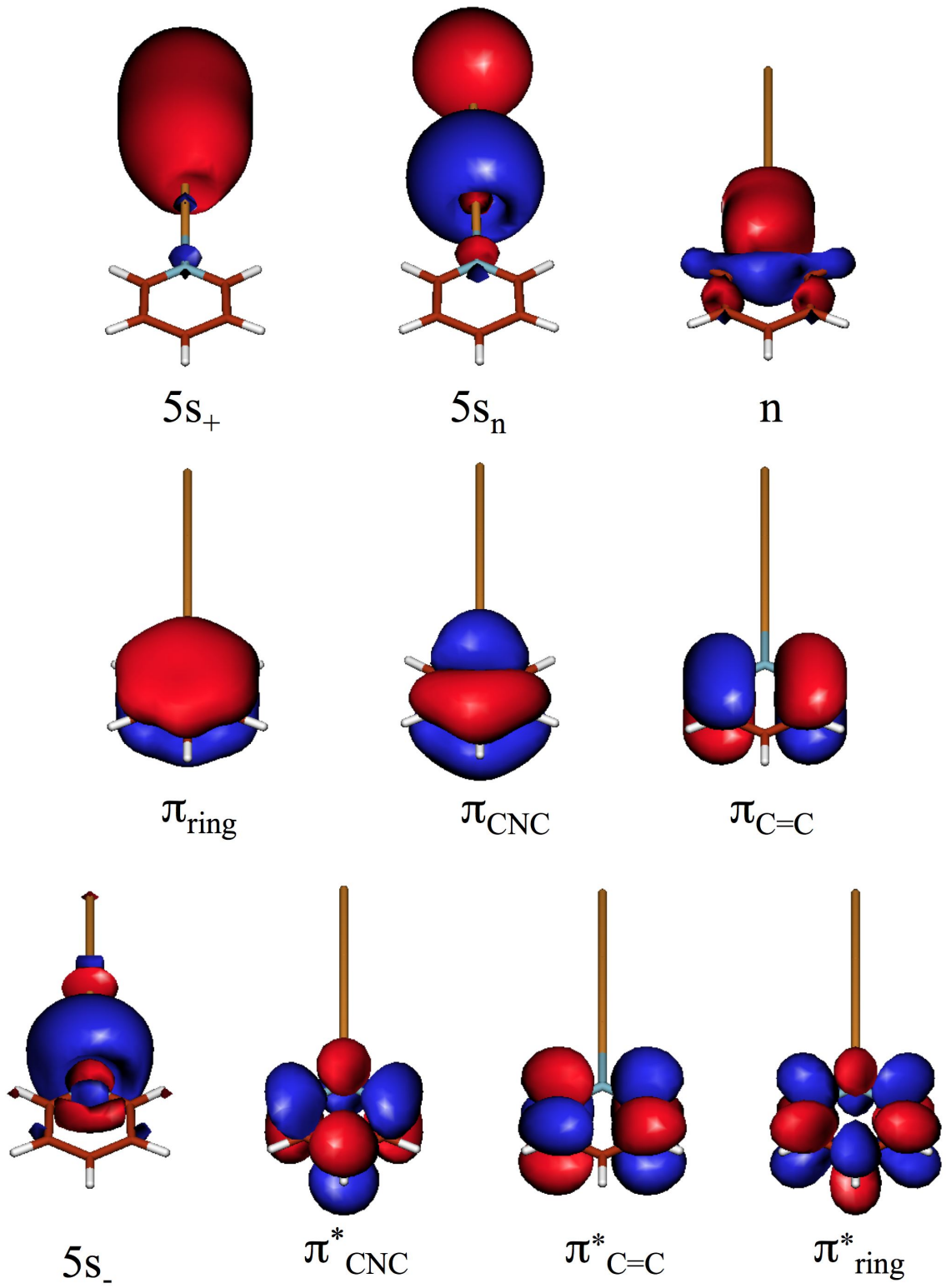

Figure.S2. Active space for Ag_3Py^q clusters

Table S1. MS-CASPT2 excitation energies (eV) of $[Ag_2\text{-}Py]^0$ cluster.[a]

State	Configuration[b]	w[c]	Q[d]	f[e]	ΔE[f]	ΔE[h]
$1A_1$	*Ref. Conf*	72	+0.1	-	-	
	$(5s+)^1(5s-)^1$	16				
$2A_1$	$(5s+)^1(5s-)^1$	68	+0.1	0.659	3.01	
	Ref. Conf	15				
$1B_1$ **CT0**	$(5s_+)^1(\pi^*_{CNC})^1$	88	-0.7	$9.0\ 10^{-05}$	**3.54**	**3.30**
$1A_2$ **CT1**	$(5s_+)^1(\pi^*_{C=C})^1$	70	-0.7	0	**4.05**	**3.95**
	$(5s_+)^1(\pi^*_{C=C})^1$	15				
$1B_2$	$(\pi_{C=C})^1(\pi^*_{CNC})^1$	49	+0.1	$2.0\ 10^{-02}$	5.22	
	$(\pi_{CNC})^1(\pi^*_{C=C})^1$	22				
$2B_1$ **S1**[g]	$(n)^1(\pi^*_{CNC})^1$	83	+0.0	$1.0\ 10^{-02}$	**5.54**	

[a]Reference active space 10 electrons in 9 orbitals. Geometry optimized at the CAS-SCF level.

[b]Reference configuration:

$(n)^2(5s_+)^2(\pi_{ping};1b_1)^2(\pi_{CNC};2b_1)^2(\pi_{C=C};1a_2)^2(5s_-)^0(\pi^*_{CNC};3b_1)^0(\pi^*_{C=C};2a_2)^0(\pi^*_{ring};4b_1)^0$

[c]Weight of the perturbatively modified wave function.

[d]Mülliken charge on the adsorbate.

[e]Oscillator strength.

[f]Excitation energy in eV.

[h]M06-HF excitation energy in eV.

[g]First excited state of the neutral pyridine.

Table S2. MS-CASPT2 excitation energies of $[Ag_3\text{-}Py]^0$ cluster.[a]

State	Configuration[b]	w[c]	Q[d]	f[e]	ΔE[f]
1^2A_1	*Ref. Conf.*	86	+0.1		
2^2A_1	$(5s_+)^1(5s_n)^2$	81	+0.2	0.12	1.34
$1B_1$ **CT0**	$(5s_n)^0(\pi^*_{CNC})^1$	81	-0.6	$3.43\ 10^{-5}$	**2.52**
3^2A_1	$(5s_n)^0(5s_-)^1$	73	+0.2	0.84	2.84
1^2A_2 **CT1**	$(5s_n)^0(\pi^*_{C=C})^1$	80	-0.7	0	**3.25**
$2B_1$ **CT0'**	$(5s_+)^1(\pi^*_{CNC})^1$	77	-0.6	$1.99\ 10^{-4}$	3.57
	$(n)^1(\pi^*_{CNC})^1$	11			
2^2A_2 **CT1'**	$(5s_+)^1(\pi^*_{C=C})^1$	87	-0.8	0	4.21
4^2A_1	$(\pi_{C=C})^1(\pi^*_{C=C})^1$	58	+0.1	$7.89\ 10^{-6}$	4.24
	$(\pi_{CNC})^1(\pi^*_{CNC})^1$	22			
1^2B_2	$(\pi_{C=C})^1(\pi^*_{CNC})^1$	78	+0.1	$2.88\ 10^{-6}$	4.36
5^2A_1	$(5s_+)^1(5s_-)^1$	79	+0.2	$4.86\ 10^{-4}$	4.37
$3B_1$ **CT0''**	$(5s_+)^1(\pi^*_{CNC})^1$	76	-0.3	$1.59\ 10^{-5}$	4.47
6^2A_1	$(\pi_{CNC})^1(\pi^*_{CNC})^1$	57	+0.1	$2.68\ 10^{-6}$	4.72
	$(\pi_{C=C})^1(\pi^*_{C=C})^1$	20			
4^2B_1 **S1**[g]	$(n)^1(\pi^*_{CNC})^1$	63	-0.2	$1.19\ 10^{-3}$	**4.86**
	$(n)^1(5s_+)^1(5s_n)^2(\pi^*_{CNC})^1$	14			

[a]Reference active space 11 electrons in 10 orbitals. Geometry optimized at the CAS-SCF level.

[b]Reference configuration:

$(n;a_1)^2(5s_+;a_1)^2\,(5s_n;a_1)^1(\pi_{ping};1b_1)^2(\pi_{CNC};2b_1)^2(\pi_{C=C};1a_2)^2(5s_-)^0(\pi^*_{CNC};3b_1)^0(\pi^*_{C=C};2a_2)^0(\pi^*_{ring};4b_1)^0$.

[c]Weight of the perturbatively modified wave function.

[d]Mülliken charge on the adsorbate.

[e]Oscillator strength.

[f]Excitation energy in eV.

[g]First excited state of isolated neutral pyridine.

Table S3. MS-CASPT2 excitation energies (eV) of $[Ag_3\text{-}Py]^-$ cluster.[a]

State	Configuration[b]	w[c]	Q[d]	f[e]	ΔE[f]	ΔE[h]
$1A_1$	Ref. Conf.	89	+0.1			
$1B_1$ **CT0**	$(5s_n)^1(\pi^*_{CNC})^1$	90	-0.7	$5.64\cdot10^{-8}$	**0.96**	**1.47**
1^1A_2 **CT1**	$(5s_n)^1(\pi^*_{C=C})^1$	90	-0.8	0	**1.51**	**1.88**
2^1B_1 **CT0'**	$(5s_+)^1(\pi^*_{CNC})^1$	90	-0.7	$3.21\cdot10^{-5}$	2.66	
2^1A_2 **CT1'**	$(5s_+)^1(\pi^*_{C=C})^1$	85	-0.76	0	3.22	
3^1B_1 **CT0'**	$(5s_n)^1(\pi^*_{ring})^1$	22	-0.7	$2.09\cdot10^{-3}$	4.65	
	$(5s_n)^1(\pi_{C=C})^1(\pi^*_{CNC})^1(\pi^*_{C=C})^1$	13				
	$(5s_n)^1(\pi_{CNC})^1(\pi^*_{CNC})^2$	-				
	$(n)^1(\pi^*_{CNC})^1$	40				
4^1B_1 **S1**[g]	$(n)^1(\pi^*_{CNC})^1$	40	0	$9.94\cdot10^{-3}$	**4.81**	
	$(5s_n)^1(\pi^*_{ring})^1$	26				
	$(5s_n)^1(\pi_{C=C})^1(\pi^*_{CNC})^1(\pi^*_{C=C})^1$	15				

[a]Reference active space 12 electrons in 10 orbitals. Geometry optimized at the CAS-SCF level.

[b]Reference configuration:

$(n;a_1)^2(5s_+;a_1)^2\,(5s_n;a_1)^2(\pi_{ping};1b_1)^2(\pi_{CNC};2b_1)^2(\pi_{C=C};1a_2)^2(5s_-)^0(\pi^*_{CNC};3b_1)^0(\pi^*_{C=C};2a_2)^0(\pi^*_{ring};4b_1)^0$.

[c]Weight of the perturbatively modified wave function.

[d]Mülliken charge on the adsorbate.

[e]Oscillator strength.

[f]Excitation energy in eV.

[g]First excited state of isolated neutral pyridine.

[h]M06-HF excitation energy in eV.

Table S4. MS-CASPT2 excitation energies (eV) of $[Ag_3\text{-}Py]^+$ cluster.[a]

State	Configuration[b]	w[c]	Q[d]	f[e]	ΔE[f]	ΔE[h]
1^1A_1	Ref. Conf.	81	+0.2			
2^1A_1	$(5s_+)^1(5s_n)^1$	81	+0.2	0.66	2.40	
2^1A_1	$(5s_+)^1(5s_n)^1$	81	+0.2	$2.76\ 10^{-5}$	2.40	
3^1A_1	$(5s_+)^0(5s_n)^2$	63	+0.2	$6.26\ 10^{-4}$	3.62	
	$(5s_+)^1(5s_-)^1$	17				
4^1A_1	$(5s_+)^1(\pi_{C=C})^1(5s_n)^1(\pi^*_{C=C})^1$	34	+0.2	$2.49\ 10^{-3}$	5.11	
	$(5s_+)^1(\pi_{CNC})^1(5s_n)^1(\pi^*_{CNC})^1$	35				
	$(5s_+)^1(5s_-)^1$	14				
5^1A_1	$(5s_+)^1(5s_-)^1$	49	+0.2	$1.92\ 10^{-4}$	5.03	
	$(5s_+)^0(5s_n)^2$	10				
	$(5s_+)^1(\pi_{C=C})^1\,(5s_n)^1(\pi^*_{C=C})^1$	25				
6^1A_1	$(5s_+)^1(\pi_{CNC})^1(5s_n)^1(\pi^*_{CNC})^1$	50	+0.2	$1.92\ 10^{-4}$	5.64	
	$(5s_+)^1(\pi_{C=C})^1(5s_n)^1(\pi^*_{C=C})^1$	25				
1^1B_2	$(\pi_{C=C})^1(\pi^*_{CNC})^1$	47	+0.2	$3.35\ 10^{-2}$	4.90	
	$(\pi_{CNC})^1(\pi^*_{C=C})^1$	19				
2^1B_2	$(5s_+)^1(\pi_{C=C})^1(5s_n)^1(\pi^*_{CNC})^1$	90	+0.2	$3.08\ 10^{-4}$	4.98	
1^1A_2 **CTi**	$(\pi_{C=C})^1(5s_n)^1$	82	+1.0	0	5.23	
1^1B_1 **CTi**	$(\pi_{CNC})^1(5s_n)^1$	82	+1.1	$1.51\ 10^{-3}$	5.39	
2^1B_1 **CT0**	$(5s_+)^1(\pi^*_{CNC})^1$	32	0.0	$2.07\ 10^{-3}$	**5.42**	**5.46**
	$(n)^1(5s_+)^1(5s_n)^1(\pi^*_{CNC})^1$	16				
	$(5s_+)^0(5s_n)^1(\pi^*_{CNC})^1$	16				
	$(n)^1(\pi^*_{CNC})^1$	12				
3^1B_1 **S1**	$(n)^1(\pi^*_{CNC})^1$	48	+0.1	$5.89\ 10^{-3}$	**5.87**	
	$(n)^1(5s_+)^1(5s_n)^1(\pi^*_{CNC})^1$	24				

[a]Reference active space 10 electrons in 10 orbitals. Geometry optimized at the CAS-SCF level.
[b]Reference configuration:
$(n;a_1)^2(5s_+;a_1)^2\,(5s_n;a_1)^0(\pi_{ping};1b_1)^2(\pi_{CNC};2b_1)^2(\pi_{C=C};1a_2)^2(5s_-)^0(\pi^*_{CNC};3b_1)^0(\pi^*_{C=C};2a_2)^0(\pi^*_{ring};4b_1)^0$.
[c]Weight of the perturbatively modified wave function.
[d]Mülliken charge on the adsorbate.
[e]Oscillator strength.
[f]Excitation energy in eV.
[g]First excited state of isolated neutral pyridine.
[h]M06-HF excitation energy in eV.

Table S5. M06-HF excitation energies (A_2 and B_1 states) of $[Ag_2\text{-}Py]^0$ cluster.

State	Sym	Configuration[a]	w[b]	Q^c	ΔE^d	f^e
S_0	1^1A_1	Ref. Conf.		0.12		
S_3	1^1B_1	$(5s_+)^1(\pi^*_{CNC})^1$	0.40	-0.34	3.30	0.1073
	(CT_0)	$(5s_+)^1(5p_+)^1$	0.07			
S_4	2^1B_1	$(5s_+)^1(5p_+)^1$	0.42	-0.17	3.48	0.1668
		$(5s_+)^1(\pi^*_{CNC})^1$	0.07			
S_5	1^1A_2	$(5s_+)^1(\pi^*_{C=C})^1$	0,5	-0.72	3.95	0.0000
	(CT_1)					
S_7	3^1B_1	$(5s_+)^1(5p_-)^1$	0,49		4.26	0.0624
S_{10}	4^1B_1	$(n + d_{z(-)})^1(\pi^*_{CNC})^1$	0.27	-0.04	5.14	0.0037
		$(n - d_{z(-)})^1(\pi^*_{CNC})^1$	0.08			
		$(n + d_{z(+)})^1(\pi^*_{CNC})^1$	0.04			
		$(n + d_{z(-)})^1(5p_+)^1$	0.02			
		$(5s_+)^1(\pi^*_{CNC})^1$	0.02			
		$(n + d_{z(-)})^1(\pi^*_{ring})^1$	0.02			
S_{13}	5^1B_1	$(5s_+)^1(6p_+)^1$	0.43		6.35	0.0123
		$(5s_+)^1(5p_+)^1$	0.01			

[a]Reference configuration:

$(n;a_1)^2(5s_+;a_1)^2\,(5s_-;a_1)^2(\pi_{\rho ing};1b_1)^2(\pi_{CNC};2b_1)^2(\pi_{C=C};1a_2)^2(5s_-)^0(\pi^*_{CNC};3b_1)^0(\pi^*_{C=C};2a_2)^0(\pi^*_{ring};4b_1)^0$.

[b]Weight of the configuration

[c]Mülliken charge on the adsorbate.

[d]Excitation energy in eV.

[e]Oscillator strength.

Table S6. M06-HF excitation energies (A_2 and B_1 states) of $[Ag_3\text{-}Py]^+$ cluster.

State	Sym	Configuration[a]	w[b]	Q^c	ΔE^d	f^e
S_0	1^1A_1	Ref. Conf.		0.21		
S_4	1^1B_1	$(5s_+)^1(5p_{x(+)})^1$	0.48	0.21	4.31	0.3613
S_6	2^1B_1	$(5s_+)^1(5p_{x(n)}+\pi^*_{CNC})^1$	0.29	0.20	4.98	0.0248
		$(5s_+)^1(\pi^*_{CNC}+5p_{x(n)})^1$	0.19			
		$(5s_+)^1(6p_x)^1$	0.01			
S_8	3^1B_1	$(n)^1(\pi^*_{CNC}+5p_{x(n)})^1$	0.18	-0.04	5.46	0.0069
	(CT_0)	$(5s_+)^1(5p_{x(n)}+\pi^*_{CNC})^1$	0.10			
		$(5s_+)^1(\pi^*_{CNC}+5p_{x(n)})^1$	0.09			
		$(n)^1(\pi^*_{CNC}+5p_{x(n)})^1$	0.05			
		$(n)^1(\pi^*_{ring})^1$	0.02			
S_{11}	4^1B_1	$(5s_+)^1(\pi^*_{CNC}+5p_{x(n)})^1$	0.15	-0.1	5.93	0.0037
	(CT_0')	$(d_{xz(-)})^1(5s_n)^1$	0.12			
		$(5s_+)^1(5p_{x(n)}+\pi^*_{CNC})^1$	0.07			
		$(n)^1(\pi^*_{CNC}+5p_{x(n)})^1$	0.06			
		$(\pi_{CNC})^1(5s_n)^1$	0.03			
		$(n)^1(5p_{x(n)}+\pi^*_{CNC})^1$	0.02			
S_{12}	5^1B_1	$(d_{xz(-)})^1(5s_n)^1$	0.23	0.03	5.98	0.0138
		$(n)^1(\pi^*_{CNC}+5p_{x(n)})^1$	0.07			
		$(5s_+)^1(\pi^*_{CNC}+5p_{x(n)})^1$	0.05			
		$(5s_+)^1(5p_{x(n)}+\pi^*_{CNC})^1$	0.03			
		$(5s_+)^1(5p_{x(-)})^1$	0.02			
		$(n)^1(5p_{x(n)}+\pi^*_{CNC})^1$	0.02			
S_{14}	1^1A_2	$(\pi_{C=C})^1(5s_n)^1$	0.44		6.07	0.0000
		$(\pi_{C=C})^1(5s_-)^1$	0.04			
S_{15}	2^1A_2	$(4d_{xy})^1(5s_n)^1$	0.43		6.14	0.0000
		$(4d_{xy})^1(5p_{z(-)})^1$	0.03			
		$(4d_{xy})^1(5p_{z(+)})^1$	0.02			
		$(4d_{xy})^1(5s_-)^1$	0.02			
S_{20}	3^1A_2	$(5s_+)^1(\pi^*_{C=C})^1$	0.47	-0.55	6.38	0.0000
	(CT_1)	$(n)^1(\pi^*_{C=C})^1$	0.03			

[a]Reference configuration:

$(n;a_1)^2(5s_+;a_1)^2\,(5s_n;a_1)^0(\pi_{ping};1b_1)^2(\pi_{CNC};2b_1)^2(\pi_{C=C};1a_2)^2(5s_-)^0(\pi^*_{CNC};3b_1)^0(\pi^*_{C=C};2a_2)^0(\pi^*_{ring};4b_1)^0$.

[b]Weight of the configuration

[c]Mülliken charge on the adsorbate.

[d]Excitation energy in eV.

[e]Oscillator strength.

Table S7. M06-HF excitation energies (A_2 and B_1 states) of $[Ag_3\text{-}Py]^-$ cluster.

State	Sym	Configuration[a]	w[b]	Q[c]	ΔE[d]	f[e]
S_0	1^1A_1	Ref. Conf.		0.06		
S_1 (CT_0)	1^1B_1	$(5s_n)^1(\pi^*_{CNC})^1$	0.42	-0.78	1.47	0.0000
		$(5s_+)^1(\pi^*_{CNC})^1$	0.07			
S_2 (CT_1)	1^1A_2	$(5s_n)^1(\pi^*_{C=C})^1$	0.43	-0.82	1.88	0.0000
		$(5s_+)^1(\pi^*_{C=C})^1$	0.06			
S_4	2^1B_1	$(5s_n)^1(5p_{x+})^1$	0.42	0.07	2.07	0.0046
		$(5s_n)^1(5p_{xn})^1$	0.04			
		$(5s_n)^1(5p_x + 5d_{xz})^1$	0.04			
S_8	3^1B_1	$(5s_n)^1(5p_{xn})^1$	0.40	0.08	2.96	0.3900
		$(5s_n)^1(5p_{x+})^1$	0.05			
		$(5s_+)^1(5p_{x+})^1$	0.03			
		$(5s_n)^1(5p_x + 5d_{xz})^1$	0.02			
S_{10}	4^1B_1	$(5s_+)^1(5p_{x+})^1$	0.34	-0.09	3.50	0.0730
		$(5s_+)^1(\pi^*_{CNC})^1$	0.08			
		$(5s_n)^1(5p_{xn})^1$	0.02			
		$(5s_+)^1(5p_x + 5d_{xz})^1$	0.02			
		$(5s_n)^1(\pi^*_{CNC})^1$	0.01			
S_{12} (CT_0')	5^1B_1	$(5s_+)^1(\pi^*_{CNC})^1$	0.31	-0.62	3.61	0.0557
		$(5s_+)^1(5p_{x+})^1$	0.10			
		$(5s_n)^1(\pi^*_{CNC})^1$	0.06			
		$(5s_+)^1(5p_{xn})^1$	0.01			
S_{14}	6^1B_1	$(5s_n)^1(5p_x + 5d_{xz})^1$	0.34	0.03	3.65	0.1803
		$(5s_+)^1(5p_{xn})^1$	0.09			
		$(5s_n)^1(5p_{xn})^1$	0.04			
		$(5s_+)^1(\pi^*_{CNC})^1$	0.02			
		$(5s_+)^1(5p_{x+})^1$	0.01			
S_{15} (CT_1')	2^1A_2	$(5s_+)^1(\pi^*_{C=C})^1$	0.43	-0.86	3.88	0,0000
		$(5s_n)^1(\pi^*_{C=C})^1$	0.06			
S_{19}	7^1B_1	$(5s_+)^1(5p_{xn})^1$	0.38	0.08	4.25	0.0074
		$(5s_n)^1(5p_x + 5d_{xz})^1$	0.08			
		$(5s_n)^1(5p_{x+})^1$	0.02			
S_{20}	8^1B_1	$(n+d_{z2(-)})^1(\pi^*_{CNC})^1$	0.15	-0.08	4.61	0.0035
		$(n+d_{z2(+)})^1(\pi^*_{CNC})^1$	0.10			
		$(n-d_{z2(n)})^1(\pi^*_{CNC})^1$	0.09			
		$(n-d_{z2(+)})^1(\pi^*_{CNC})^1$	0.07			
		$(5s_+)^1(\pi^*_{CNC})^1$	0.01			
		$(n+d_{z2(-)})^1(\pi^*_{ring})^1$	0.01			
S_{23}	9^1B_1	$(5s_+)^1(5p_x + 5d_{xz})^1$	0.46	0.07	5.01	0.0250
		$(5s_+)^1(5p_{x+})^1$	0.01			

[a]Reference configuration:

$(n;a_1)^2(5s_+;a_1)^2\,(5s_n;a_1)^2(\pi_{ping};1b_1)^2(\pi_{CNC};2b_1)^2(\pi_{C=C};1a_2)^2(5s_-)^0(\pi^*_{CNC};3b_1)^0(\pi^*_{C=C};2a_2)^0(\pi^*_{ring};4b_1)^0$.

[b]Weight of the configuration

[c]Mülliken charge on the adsorbate.

[d]Excitation energy in eV.

[e]Oscillator strength.

Table S8. M06-HF excitation energies (A_2 and B_1 states) of $[Ag_n\text{-}Py]^q$ clusters.

Cluster	State	Configuration	w[a]	Q^b	ΔE^c	f^d
Ag_3^-	GS (S_0) 1^1A_1	*Ref. Conf.*		0.06		
	CT_0 (S_1) 1^1B_1	$(5s_n)^1(\pi^*_{CNC})^1$	0.42	-0.78	1.47	0.0000
		$(5s_+)^1(\pi^*_{CNC})^1$	0.07			
	CT_1 (S_2) 1^1A_2	$(5s_n)^1(\pi^*_{C=C})^1$	0.43	-0.82	1.88	0.0000
		$(5s_+)^1(\pi^*_{C=C})^1$	0.06			
	S_1 (S_{20}) 8^1B_1	$(n+d_{z2(-)})^1(\pi^*_{CNC})^1$	0.15	-0.08	4.61	0.0035
		$(n+d_{z2(+)})^1(\pi^*_{CNC})^1$	0.10			
Ag_5^-	GS (S_0) 1^1A_1	Ref. Conf.		0.07		
	CT_0 (S_2) 1^1B_1	$(5s_n)^1(\pi^*_{CNC})^1$	0.34	-0.73	2.00	0.0004
		$(5s_{+-})^1(\pi^*_{CNC})^1$	0.11			
	CT_1 (S_5) 1^1A_2	$(5s_n)^1(\pi^*_{C=C})^1$	0.37	-0.79	2.45	0.0000
		$(5s_{+-})^1(\pi^*_{C=C})^1$	0.10			
	S_1 (S_{31}) 12^1B_1	$(n)^1(\pi^*_{CNC})^1$	0.15	-0.19	4.82	0.0005
Ag_7^-	GS (S_0) 1^1A_1	Ref. Conf.		0.09		
	CT_0 (S_2) 1^1B_1	$(5s_n)^1(\pi^*_{CNC})^1$	0.27	-0.68	2.37	0.0013
		$(5s_{+-+})^1(\pi^*_{CNC})^1$	0.13			
	CT_1 (S_9) 1^1A_2	$(5s_n)^1(\pi^*_{C=C})^1$	0.3	-0.77	2.85	0.0000
		$(5s_{+-+})^1(\pi^*_{C=C})^1$	0.13			
	S_1 (S_{44}) 16^1B_1	$(n)^1(\pi^*_{CNC})^1$	0.21	-0.09	4.94	0.0051
Ag_2^0	GS (S_0) 1^1A_1	Ref. Conf.		0.12		
	CT_0 (S_3) 1^1B_1	$(5s_+)^1(\pi^*_{CNC})^1$	0.40	-0.34	3.30	0.1073
		$(5s_+)^1(5p_+)^1$	0.07			
	CT_1 (S_5) 1^1A_2	$(5s_+)^1(\pi^*_{C=C})^1$	0.5	-0.72	3.95	0.0000
	S_1 (S_{10}) 4^1B_1	$(n + d_{z(-)})^1(\pi^*_{CNC})^1$	0.27	-0.04	5.14	0.0037
Ag_7^+	GS (S_0) 1^1A_1	Ref. Conf.		0.18		
	CT_0 (S_{21}) 7^1B_1	$(5s_{+-+})^1(\pi^*_{CNC})^1$	0.16	-0.24	4.86	0.0150
	CT_1 (S_{27}) 1^1A_2	$(5s_{+-+})^1(\pi^*_{C=C})^1$	0.34	-0.64	5.51	0.0000
		$(5s_{+-})^1(\pi^*_{C=C})^1$	0.13			
	S_1 (S_{33}) 11^1B_1	$(n)^1(\pi^*_{CNC})^1$	0.23	0.00	5.62	0.0027
Ag_5^+	GS (S_0) 1^1A_1	Ref. Conf.		0.19		
	CT_0 (S_{14})	$(5s_{+-})^1(\pi^*_{CNC})^1$	0.29	-0.34	5.08	0.0072
		$(5s_{++})^1(\pi^*_{CNC})^1$	0.08			
		$(n)^1(\pi^*_{CNC})^1$	0.06			
	CT_1 (S_{22})	$(5s_{+-})^1(\pi^*_{C=C})^1$	0.41	-0.62	5.80	0.0000
		$(5s_{++})^1(\pi^*_{C=C})^1$	0.08			
	S_1 (S_{19})	$(n)^1(\pi^*_{CNC})^1$	0.25	-0.04	0.00	0.0013
		$(5s_{+-})^1(\pi^*_{C=C})^1$	0.08			
Ag_3^+	GS (S_0) 1^1A_1	Ref. Conf.		0.21		
	CT_0 (S_{11}) 4^1B_1	$(5s_+)^1(\pi^*_{CNC} + 5p_{x(n)})^1$	0.15	-0.1	5.93	0.0037
		$(d_{xz(-)})^1(5s_n)^1$	0.12			
	CT_1 (S_{20}) 3^1A_2	$(5s_+)^1(\pi^*_{C=C})^1$	0.47	-0.55	6.38	0.0000
		$(n)^1(\pi^*_{C=C})^1$	0.03			
	S_1 (S_8) 3^1B_1	$(n)^1(\pi^*_{CNC} + 5p_{x(n)})^1$	0.18	-0.04	5.46	0.0069
		$(5s_+)^1(5p_{x(n)} + \pi^*_{CNC})^1$	0.10			

[a]Weight of the configuration.

[b]Mülliken charge on the adsorbate.

[c]Excitation energy in eV.

[d]Oscillator strength.