SUPPORTING INFORMATION

Franck-Condon dominates the Surface-Enhanced Raman Scattering of 3-methylpyridine: Propensity Rules of the Charge Transfer Mechanism under Reduced Symmetry

Silvia P. Centeno, Isabel López-Tocón, Jessica Roman-Perez,

Juan F. Arenas, Juan Soto, Juan C. Otero*

Department of Physical Chemistry, Faculty of Science, University of Málaga, E-29071

Málaga, Spain.

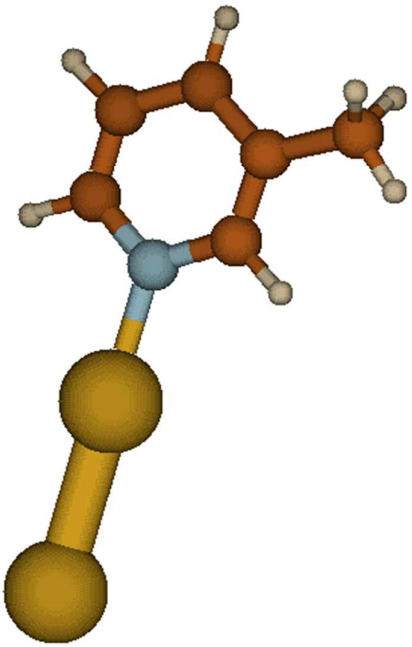

Figure S1: RHF/LanL2DZ optimized geometry of the Ag_2-3-methylpyridine complex in the S_0;^{1}A' ground electronic state.

Table S1: Experimental and scaled vibrational wavenumbers (cm^{-1}), relative intensities and assignment of the Raman of the aqueous solution and SERS spectra of 3-methylpyridine.

Raman Solution		Scaled[a]	SERS (Electrode Potential)							
			-0.25 V		-0.50 V		-0.75 V			
ν	I	ν	ν	I	ν	I	ν	I	PED[a]	Assignment
		3074							98 ν(CH)	ν(CH);A'
3076	380	3053	3061	202	3061	71	3055	24	100 ν(CH)	ν(CH);A'
		3046	3044	168	3037	52	3033	14	99 ν(CH)	ν(CH);A'
		3035							99 ν(CH)	ν(CH);A'
		2976					2976	16	99 $\nu(CH_3)$	$\nu(CH_3)$;A'
		2958							100 $\nu(CH_3)$	$\nu(CH_3)$;A"
2937	420	2912	2923	243	2923	100	2919	56	100 $\nu(CH_3)$	$\nu(CH_3)$;A'
1602	200	1597	1602	215	1600	98	1598	128	62 ν_{ring}, 23 δ(CH)	8b;ν_{ring};A'
1584	100	1578	1584	100	1583	100	1578	100	66 ν_{ring}, 19 δ(CH)	8a;ν_{ring};A'
		1486					1478	12	31 ν_{ring}, 62 δ(CH)	19a,δ(CH);A'
		1455							64 $\delta_{as}(CH_3)$, 14 δ(CH)	$\delta_{as}(CH_3)$;A'
		1450							92 $\delta_{as}(CH_3)$	$\delta_{as}(CH_3)$;A"
		1418			1414	9	1412	16	34 ν_{ring}, 34 δ(CH)	19b,δ(CH);A'
1388	140	1378			1384	23	1382	16	90 $\delta_{as}(CH_3)$	$\delta_s(CH_3)$;A'
		1354							92 δ(CH)	δ(CH);A'
		1240							68 ν_{ring}, 21 δ(CH)	14;ν_{ring};A'
1231	720	1219	1233	144	1231	89	1230	69	55 ν_{ring}, 13 δ(CH)	ν(CX);A'
1193	240	1200	1195	144	1193	112	1192	174	46 ν_{ring}, 41 δ(CH)	δ(CH);A'
1121	140	1124							52 ν_{ring}, 39 δ(CH)	ν_{ring};A'
		1051							67 $r(CH_3)$, 16 γ(CH)	$r(CH_3)$;A"
1049	960	1039	1053	317	1053	168	1049	132	67 ν_{ring}, 19 12;δ_{ring}	ν_{ring};A'
1035	2000	1024	1035	2231	1033	748	1033	459	32 ν_{ring}, 50 12;δ_{ring}	12;δ_{ring};A'
						-283[b]		*-63*[b]	*ν(CH₃) as ref. band*	12;δ_{ring};A'
						-53[c]		*222*[c]	*ν(CH) as ref. band*	12;δ_{ring};A'
		995			996	9	922	11	77 γ(CH), 12 16a;τ_{ring}	γ(CH);A"
		980							63 $r(CH_3)$, 26 ν_{ring}	$r(CH_3)$;A'
		937			938	14	934	14	78 γ(CH)	γ(CH);A"
		924							88 γ(CH)	γ(CH);A"
810	560	792	816	217	816	140	814	86	38 δ_{ring}, 31 ν_{ring}	1;ν_{ring};A'
		787							83 γ(CH)	γ(CH);A"
		702			706	9	704	8	71 4;τ_{ring}, 17 γ(CH)	4;τ_{ring};A"
640	120	632	648	107	646	93	644	80	61 6a;δ_{ring}, 24 6b;δ_{ring}	6a; δ_{ring};A'
537	780	534	538	59	538	42	538	54	39 6b;δ_{ring}, 29 6a;δ_{ring}	6b;δ_{ring};A'
		458			461	9	461	10	55 γ(CX), 29 τ_{ring}	γ(CX);A"
		406	403	44	401	9	401	10	53 16b;τ_{ring}, 29 16a;τ_{ring}	16b;τ_{ring};A"
		349			349	5	345	10	80 δ(CX)	δ(CX);A'
		204							56 τ_{ring}, 22 γ(CX)	16a;τ_{ring};A"
		64							75 τ(CX)	τ(CX);A"

[a]Scaled wavenumbers and % Potencial Energy Distribution (PED) from the SQMFF.[13] [b,c]$I_{SERS-CT}$ intensities of mode 12 obtained from equation (3) by subtracting the intensities of the SERS at -0.25 V and taking the CH_3 or CH stretching bands as internal references, respectively.

Table S2: Experimental wavenumbers shifts ($\Delta\nu$,cm^{-1}) between the SERS spectrum of 3-methylpyridine (3MP) recorded at -0.50 V and the Raman of the pure liquid (Ra: ν,cm^{-1}) and RHF/LanL2DZ calculated shifts for the vibrations of the Ag_2-3MP surface complex with respect to those of the isolated 3MP.

	Experimental		Calculated	
	Ra		3MP	
Assignment	ν	$\Delta\nu^a$	ν	$\Delta\nu^b$
ν(CH), A'	3089	-	3431	+7
ν(CH), A'	3057	+4	3409	+9
ν(CH), A'	3037	-	3385	+8
$\nu(CH_3)$, A'	2980	-	3296	+6
$\nu(CH_3)$, A'	2924	-1	3201	+5
8b,ν_{ring}, A'	1597	+3	1788	+3
8a,ν_{ring}, A'	1576	+7	1761	+6
19a,δ(CH), A'	1480	-2	1636	+2
$\delta(CH_3)$, A'	1456	-	1649	+2
19b,δ(CH), A'	1412	+2	1571	+4
$\delta_s(CH_3)$, A'	1384	0	1581	+3
ν(CX), A'	1227	-	1363	+4
14,ν_{ring}, A'	-	-	1291	+2
δ(CH), A'	1189	+4	1328	+1
ν_{ring}, A'	1125	-	1225	0
ν_{ring}, A'	1041	+8	1134	+3
12,δ_{ring}, A'	1029	+4	1137	+12
1,ν_{ring}, A'	806	+10	869	+7
6a,δ_{ring}, A'	630	+16	696	+13
6b,δ_{ring}, A'	535	+3	584	0
16b,τ_{ring}, A''	401	0	468	+2
δ(CX), A'	339	+10	364	+6

[a] ν(-0.5V SERS) – ν(liquid Raman); [b] $\nu(Ag_2$-3MP) – ν(3MP).

Table S3: CIS/LanL2DZ calculated vertical excitation energies (ΔE), oscillator strengths (*f*) and Mulliken charges (*q*) corresponding to the Franck-Condon points of the first ten excited singlets of the Ag_2-3-methylpyridine complex. The respective values for the optimized CT_i states are shown in brackets.

State:	S_0 $1\,^1A'$	S_1 $2\,^1A'$	S_2 $3\,^1A'$	S_3 $1\,^1A''$	S_4 $4\,^1A'$	S_5 $2\,^1A''$	$S_6(CT_0)$ $3\,^1A''$	S_7 $5\,^1A'$	S_8 $6\,^1A'$	$S_9(CT_1)$ $4\,^1A''$	S_{10} $7\,^1A'$
$\Delta E(S_i\text{-}S_0)$/eV	0	2.99	3.23	3.28	4.21	4.23	4.34 (3.77)	4.67	5.12	5.17 (4.71)	6.27
f		0.731	0.423	0.452	0.021	0.016	0.001	0.039	0.227	0.000	0.099
Ag_2 charge *q*	-0.06	-0.09	-0.09	-0.08	-0.12	-0.10	0.75 (0.61)	-0.20	-0.11	0.82 (0.76)	-0.07
$\Delta q=q_{S0}-q_{Si}$ [a]	0	+0.03	+0.03	+0.02	+0.06	+0.04	-0.81 (-0.67)	+0.14	0.05	-0.88 (-0.82)	+0.01

[a] Transferred charge from the Ag_2 cluster to 3-methylpyridine in the S_i state.

Table S4: Calculated ΔQ displacements (equation 1, $amu^{1/2}$ Å) and relative SERS-CT intensities (equation 2) related to the D_0-S_0 transition of isolated 3-methylpyridine and the CT_i-S_0 transitions of the Ag_2-3-methylpyridine surface complex.

Method:			HF/LanL2DZ		CIS/LanL2DZ			
Transition:			D_0-S_0 $2A''$-$1A'$		$S_6(CT_0)$-S_0 $3^1A''$-$^1A'$		$S_9(CT_1)$-S_0 $4^1A''$-$^1A'$	
Symmetry	Mode	ν_{scaled}	ΔQ	I	ΔQ	I	ΔQ	I
A'	ν(CH)	3074	-0.008	3.4	0.001	0.0	-0.006	2.8
A'	ν(CH)	3053	-0.003	<1	0.001	0.0	-0.001	<1
A'	ν(CH)	3046	0.004	<1	0.001	0.0	0.002	<1
A'	ν(CH)	3035	0.003	<1	-0.004	1.8	0.005	1.9
A'	$\nu(CH_3)$	2976	0.000	0.0	-0.001	0.0	0.000	0.0
A'	$\nu(CH_3)$	2912	-0.008	2.8	0.003	1.0	0.008	4.5
A'	8b,ν_{ring}	1597	-0.099	**75.0**	-0.081	**100.0**	0.088	**100.0**
A'	8a,ν_{ring}	1578	-0.118	**100.0**	0.075	**83.1**	-0.086	**90.4**
A'	19a,δ(CH)	1486	-0.027	4.1	0.007	<1	-0.025	6.4
A'	$\delta_{as}(CH_3)$	1455	0.004	<1	-0.006	<1	-0.002	0.0
A'	19b,δ(CH)	1418	0.006	<1	0.001	0.0	0.017	2.6
A'	$\delta_s(CH_3)$	1378	0.001	0.0	0.004	<1	-0.027	4.5
A'	δ(CH)	1354	0.026	3.0	0.018	3.1	-0.016	2.0
A'	ν(CX)	1219	-0.087	**21.3**	-0.088	**45.6**	0.007	<1
A'	14,ν_{ring}	1240	-0.003	0.0	-0.025	4.3	0.046	12.1
A'	δ(CH)	1200	0.130	**52.5**	-0.105	**69.8**	0.019	2.0
A'	ν_{ring}	1124	-0.031	2.3	0.059	17.2	0.007	<1
A'	ν_{ring}	1039	-0.025	1.2	-0.092	**33.3**	-0.155	**78.3**
A'	12,δ_{ring}	1024	0.130	**33.1**	0.084	**29.0**	0.067	15.2
A'	$r(CH_3)$	980	0.038	2.6	0.013	<1	-0.039	4.7
A'	1,ν_{ring}	792	-0.177	**27.2**	-0.111	**22.2**	-0.129	**25.0**
A'	6a,δ_{ring}	632	-0.163	11.9	-0.110	11.6	-0.006	<1
A'	6b,δ_{ring}	534	0.042	<1	-0.034	<1	0.089	3.5
A'	δ(CX)	349	0.041	0.0	0.041	<1	0.014	3.5

IMDHO method for calculating resonant Raman intensities:

SERS-CT spectra have been calculated according with the independent mode displaced harmonic oscillator (IMDHO) method,[1,2] where it is assumed that the excited-state displacements with respect to the ground state geometry are proportional to the gradient of the excited state potential energy surface. To be specific, it is assumed that the intensity of a Raman band in preresonance conditions is proportional to the dimensionaless shift parameter of Manneback[3] [Eq. (1)] and this shift parameter is calculated within the harmonic approximation[1] [Eq. (2)].

$$I_i \propto \gamma_i \omega_i^2 \tag{2}$$

$$\gamma_i = B_i^2 \tag{3}$$

where B_i is the adimensional shift parameter given by [Eq.(3)]

$$B_i = \frac{1}{\sqrt{2}}\left(\frac{c}{4\pi^2 h}\right)^{1/2} \frac{1}{c^2} \nu^{-3/2} \boldsymbol{f} \cdot \mathbf{M}^{-1/2} \mathbf{L}_i \tag{4}$$

$\boldsymbol{f}$ is the gradient vector of the excited state evaluated at the Franck-Condon geometry, $\mathbf{M}$ is the diagonal matrix of atomic masses and $\mathbf{L}_i$ is the eigenvector of the Hessian matrix associated with the *i*-normal mode.

1. F. Zerbetto and M. Z. Zgierski, *J. Chem. Phys.* 1994, **101**, 1842.

2. F. Avila, J. Soto, J. F. Arenas, J. A. Rodríguez, D. Peláez and J. C. Otero, *J. Phys. Chem. C*, 2009, **113**, 105.

3. C. Manneback, *Physica*, 1951, **17,** 1001.

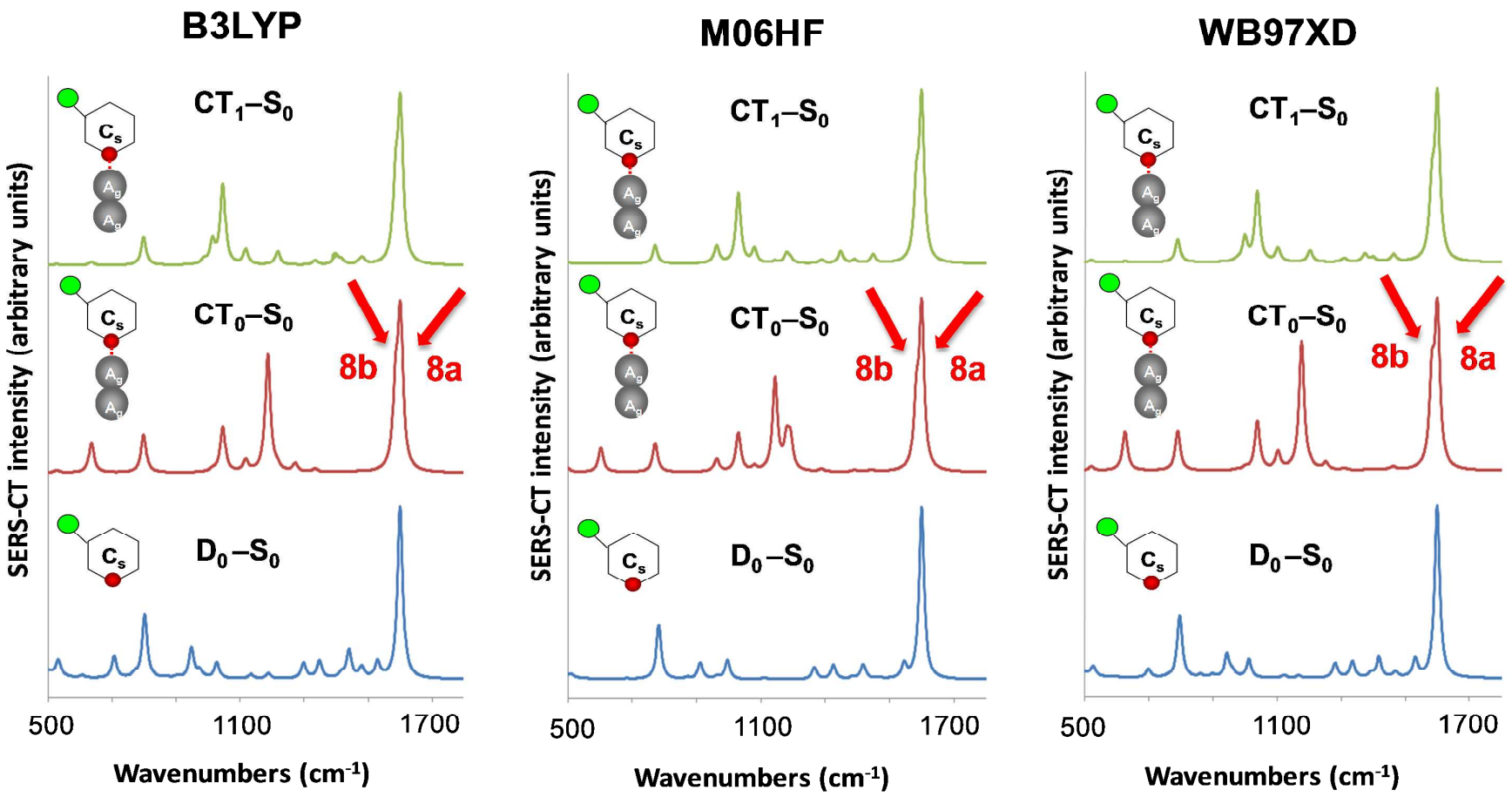

Figure S2: IMDHO-DFT and TDDFT calculated SERS relative intensities for the D_0-S_0 electronic *transition* of the isolated molecule and CT_0-S_0 and CT_1-S_0 transitions of the 3-methylpyridine-Ag_2 surface complex, respectively. These calculations have been carried out with B3LYP, M06HF and wB97XD functionals and a hybrid LanL2DZ/6-31G* basis set for Ag/3MP systems, respectively. The vibrational wavenumbers of the bands are scaled in order to locate the respective 8a/8b bands at 1600 cm^{-1}.

Table S5: B3LYP, M06HF and WB97XD calculated vertical excitation energies (ΔE) with LanL2DZ/6-31G* basis set for Ag/3MP systems, respectively, oscillator strengths (*f*) and Mulliken charges (*q*) corresponding to the Franck-Condon points of the first ten excited singlets of the Ag_2-3-methylpyridine complex.

B3LYP

State:	S_0 $1\ ^1A'$	$S_1(CT_0)$ $1\ ^1A''$	$S_2(CT_1)$ $2\ ^1A''$	S_3 $2\ ^1A'$	S_4 $3\ ^1A'$	S_5 $3\ ^1A''$	$S_6(CT_2)$ $4\ ^1A''$	S_7 $4\ ^1A'$	S_8 $5\ ^1A'$	S_9 $6\ ^1A''$	S_{10} $5\ ^1A''$
$\Delta E(S_i\text{-}S_0)$/eV	0	2.47	2.97	3.27	3.96	4.08	4.58	4.67	4.82	4.86	4.91
f		0.001	0.000	0.598	0.266	0.316	0.007	0.003	0.033	0.005	0.002
Ag_2 charge *q*	-0.19	0.56	0.59	-0.21	-0.23	-0.24	0.36	-0.26	-0.21	-0.26	-0.23
$\Delta q=q_{S0}-q_{Si}$[a]	0	-0.75	-0.78	0.02	0.04	0.05	-0.55	0.07	0.02	0.07	0.04

M06HF

State:	S_0 $1\ ^1A'$	S_1 $2\ ^1A'$	S_2 $3\ ^1A'$	S_3 $1\ ^1A''$	$S_4(CT_0)$ $2\ ^1A''$	S_5 $4\ ^1A'$	S_6 $3\ ^1A''$	S_7 $5\ ^1A'$	$S_8(CT_1)$ $4\ ^1A''$	S_9 $6\ ^1A'$	$S_{10}(CT_2)$ $5\ ^1A''$
$\Delta E(S_i\text{-}S_0)$/eV	0	2.86	3.28	3.36	3.96	4.18	4.26	4.35	4.55	4.94	5.44
f		0.537	0.230	0.260	0.003	0.063	0.057	0.000	0.000	0.138	0.003
Ag_2 charge *q*	-0.15	-0.17	-0.19	-0.17	0.50	-0.18	-0.16	-0.27	0.64	-0.16	0.03
$\Delta q=q_{S0}-q_{Si}$[a]	0	0.02	0.04	0.02	-0.65	0.03	0.01	0.12	-0.80	0.01	-0.18

WB97XD

State:	S_0 $1\ ^1A'$	S_1 $2\ ^1A'$	$S_2(CT_0)$ $1\ ^1A''$	S_3 $3\ ^1A'$	S_4 $2\ ^1A''$	$S_5(CT_1)$ $3\ ^1A''$	S_6 $4\ ^1A'$	S_7 $5\ ^1A'$	S_8 $4\ ^1A''$	S_9 $5\ ^1A''$	S_{10} $6\ ^1A''$
$\Delta E(S_i\text{-}S_0)$/eV	0	3.28	3.68	3.90	4.02	4.35	5.08	5.11	5.12	5.26	5.26
f		0.607	0.045	0.319	0.309	0.002	0.008	0.048	0.001	0.023	0.000
Ag_2 charge *q*	-0.18	-0.19	0.47	-0.23	-0.12	0.61	-0.23	-0.22	-0.23	-0.15	0.18
$\Delta q=q_{S0}-q_{Si}$[a]	0	0.01	-0.65	0.05	-0.06	-0.79	0.05	0.04	0.05	-0.03	0.00

[a]Transferred charge from the Ag_2 cluster to 3-methylpyridine in the S_i state.