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Electronic Supplementary Information (ESI)

Charge transfer at the nanoscale and the role of the out-of-plane vibrations in the selection rules of surface-enhanced Raman scattering

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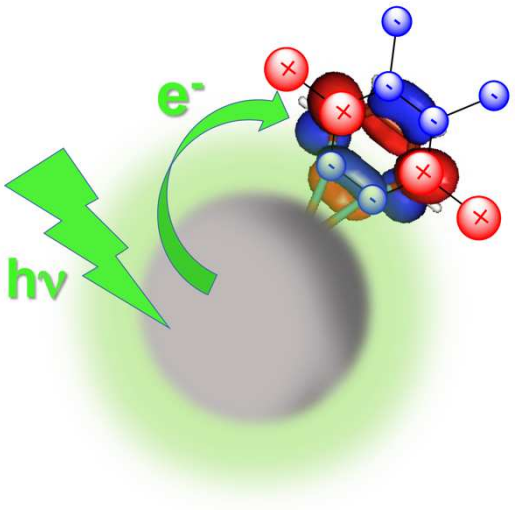


Table S1 Assignment of the infrared and Raman spectra (cm^{-1}) of pure liquid and 1M aqueous solution of pyridazine and the scaled B3LYP/6-31+G* calculated wavenumbers.

Liquid		Solution		
IR	Ra	Ra	B3LYP/ 6-31+G*	
ν [a]	ν	ν	ν[b]	Asignment[c]
3085	-	-	3120	2;ν(CH),A_1
3068	3068	3086	3111	20a;ν(CH),B_2
3056	3056	3074	3103	7a;ν(CH),A_1
-	-	-	3095	13;ν(CH),B_2
1570	1568	1574	1570	8a;ν_{ring},A_1
1563	1566	-	1565	8b;ν_{ring},B_2
1446	1448	1458	1443	19b;δ(CH),A_1
1415	-	-	1404	19a;δ(CH),B_2
1283	1287	1293	1281	δ(CH),B_2
1159	1162	1186	1167	14;ν_{ring},A_1
-	-	1166	-	16b+11,A_1
-	1118	1124	1144	δ(CH),A_1
1061	1063	1069	1064	ν_{ring},A_1
1058	-	-	1055	ν_{ring},B_2
-	-	-	1022	12;δ_{ring},B_2
-	-	-	1006	5;γ(CH),A_2
-	-	-	970	17b;γ(CH),B_1
963	965	975	983	1;ν_{ring},A_1
-	-	-	934	10b;γ(CH),A_2
760	756	758	754	11;γ(CH),B_1
-	-	-	753	4;τ_{ring},A_2
664	666	668	659	6a;δ_{ring},A_1
629	626	634	612	6b;δ_{ring},B_2
372	375	375	372	16b;τ_{ring},B_1
-	367	-	370	16a;τ_{ring},A_2

[a]From A.R. Bérces, P.G. Szalay, I. Magdó, G. Fogarasi, and G. Pongor, *J. Phys. Chem.* 1993, **97**, 1356-1363. [b]Calculated in-plane and out-of-plane wavenumbers scaled by 0.97 and 0.99, respectively. [c]Wilson's nomenclature from G. Varsanyi, Vibrational spectra of benzene derivatives, Academic Press, New York, 1969. ν:stretching, δ:in-plane deformation, γ:out-of-plane deformation and τ:torsion.

Table S2 Assignment of the SERS spectra (cm^{-1}) of pyridazine recorded at different electrode potentials correlated with the experimental (Raman) and the B3LYP/6-31+G* scaled wavenumbers.

Exp.	B3LYP/	SERS (Electrode Potential/V)				
Raman	6-31+G*	0.00	–0.25	–0.50	–0.75	
ν^a	ν^b	ν	ν	ν	ν	Assignment[e]
-	3120	-	-	-	-	$2;\nu(CH),A_1$
3086	3111	-	-	-	-	$20a;\nu(CH),B_2$
3074	3103	3064	3064	3062	3062	$7a;\nu(CH),A_1$
-	3095	-	-	-	-	$13;\nu(CH),B_2$
1574	1570	1576	1574	1574	1574	$8a;\nu_{ring},A_1$
1566[c]	1565	-	-	-	-	$8b;\nu_{ring},B_2$
1458	1443	1456	1454	1454	1452	$19b;\delta(CH),A_1$
1413[d]	1404	-	-	-	-	$19a;\delta(CH),B_2$
1293	1281	-	1293	1289	1289	$\delta(CH),B_2$
1186	1167	1207	1207	1209	1209	$14;\nu_{ring},A_1$
1166	-	1170	1166	1166	1166	$16b+11,A_1$
1124	1144	1152	1154	sh	-	$\delta(CH),A_1$
1069	1064	1069	1069	1067	1063	ν_{ring},A_1
1049[d]	1055	-	-	-	-	ν_{ring},B_2
1014[d]	1022	-	-	-	-	$12;\delta_{ring},B_2$
-	1006	-	-	-	-	$5;\gamma(CH),A_2$
987[d]	970	-	1001	997	999	$17b;\gamma(CH),B_1$
975	983	981	979	975	971	$1;\nu_{ring},A_1$
943[d]	934	-	941	943	-	$10b;\gamma(CH),A_2$
758	754	776	774	774	760	$11;\gamma(CH),B_1$
729[d]	753	722	746	744	740	$4;\tau_{ring},A_2$
668	659	670	670	670	670	$6a;\delta_{ring},A_1$
634	612	644	642	640	640	$6b;\delta_{ring},B_2$
375	372	389	387	385	379	$16b;\tau_{ring},B_1$
367[c]	370	-	-	-	-	$16a;\tau_{ring},A_2$

[a]1M aqueous solution (this work). [b]Calculated wavenumbers for in-plane and out-of-plane fundamentals scaled by 0.97 and 0.99, respectively. [c]Pure liquid (this work). [d]Pure liquid from. J. Vázquez, J.J. López González, F. Márquez and J. E. Boggs, *J. Raman Spectrosc*. 1998, **29** 547-559. [e]Wilson's nomenclature from G. Varsanyi, Vibrational spectra of benzene derivatives, Academic Press, New York, 1969. ν:stretching, δ:in-plane deformation, γ:out-of-plane deformation and τ:torsion.

Table S3 B3LYP/LanL2DZ calculated wavenumber shifts ($\Delta\nu/cm^{-1}$) of the vibrations of pyridazine (Pdz) in the Pdz-Ag_2 and Pdz-Ag^+ complexes with C_{2v} and C_s symmetry.

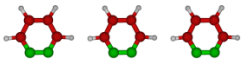
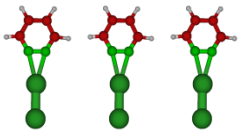
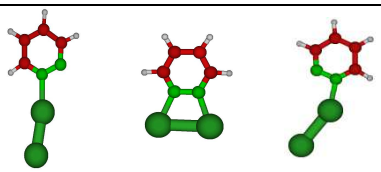
		B3LYP/ 6-31+G*	B3LYP/LanL2DZ				
		Pdz	Pdz	Pdz-$Ag_2(C_{2v})$	Pdz-$Ag_2(C_s)$	Pdz-$Ag^+(C_{2v})$	Pdz-$Ag^+(C_s)$
Symmetry[a]	Assignment[b]	ν[c]	ν	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$
A_1	2;ν(CH)	3120	3250	6	8	19	20
	7a;ν(CH)	3103	3224	9	12	26	27
	8a;ν_{ring}	1570	1596	3	4	10	6
	19b;δ(CH)	1443	1455	4	8	9	11
	14;ν_{ring}	**1167**	**1198**	**12**	**14**	**60**	**48**
	δ(CH)	**1144**	**1161**	**21**	**21**	**43**	**41**
	ν_{ring}	1064	1067	0	5	-4	-4
	1;ν_{ring}	975	962	-3	10	-20	-3
	6a;δ_{ring}	668	675	6	6	14	13
B_2	20a;ν(CH)	3111	3236	8	10	23	24
	13;ν(CH)	3095	3214	9	12	29	29
	8b;ν_{ring}	1565	1576	4	10	7	9
	19a;δ(CH)	1404	1425	7	7	18	16
	δ(CH)	1281	1303	4	8	5	12
	ν_{ring}	1055	1080	2	8	10	17
	12;δ_{ring}	1022	1036	14	22	30	45
	6b;δ_{ring}	612	629	3	13	9	16
A_2	5;γ(CH)	1006	1041	4	3	15	14
	10b;γ(CH)	934	940	11	8	28	20
	4;τ_{ring}	753	774	-1	-5	-11	-16
	16a;τ_{ring}	370	380	6	16	9	16
B_1	17b;γ(CH)	970	986	10	9	28	23
	11;γ(CH)	754	778	5	7	18	20
	16b;τ_{ring}	372	374	7	8	23	27

[a]C_{2v} symmetry. [b]Wilson's nomenclature from G. Varsanyi, Vibrational spectra of benzene derivatives, Academic Press, New York, 1969. ν:stretching, δ:in-plane deformation, γ:out-of-plane deformation and τ:torsion. [c]Calculated wavenumbers for in-plane and out-of-plane fundamentals scaled by 0.97 and 0.99, respectively.

Table S4 M06-HF/LanL2DZ vertical excitation energies (ΔE/eV, symmetries of the isolated molecules) for the two first CT electronic transitions of the corresponding molecule-Ag_2 complex.

	Vertical Energies / eV		
	Pyridine-Ag_2	Pyrazine-Ag_2	Pyridazine-Ag_2
ΔE (CT_0-S_0)	3.29 (**$B_1 \leftarrow A_1$**)	2.90 (**$B_{3u} \leftarrow A_g$**)	2.61 (**$A_2 \leftarrow A_1$**)
ΔE (CT_1-S_0)	3.94 (**$A_2 \leftarrow A_1$**)	3.73 (**$A_u \leftarrow A_g$**)	3.12 (**$B_1 \leftarrow A_1$**)

Table S5 M06-HF/LanL2DZ optimized structures of pyridazine (Pdz) and of Pdz-Ag_2 complexes in the ground electronic state (S_0;$^1A_1$) and the corresponding doublet states (D_0 and D_1) of Pdz^- and the singlet CT states (CT_0 and CT_1) of the complexes, respectively.

	Pdz (C_{2v})			**Pdz-Ag_2 (C_{2v})**			**Pdz-Ag_2 (C_s)**		
Parameter[a]	S_0	D_0	D_1	S_0	CT_0	CT_1	S_0	CT_0	CT_1
Structure									
R_1	1.346	1.435	1.308	1.349	1.432	1.342	1.345	1.408	1.317
$R_{2/3}$	1.344	1.360	1.399	1.336	1.354	1.361	1.338/1.348	1.367	1.344/1.375
$R_{4/5}$	1.408	1.394	1.446	1.412	1.386	1.464	1.410/1.410	1.376	1.468/1.434
R_6	1.391	1.448	1.376	1.389	1.454	1.364	1.390	1.456	1.363
$R_{7/8}$	1.081	1.088	1.079	1.081	1.082	1.075	1.081/1.080	1.082	1.076/1.075
$R_{9/10}$	1.082	1.083	1.086	1.082	1.079	1.082	1.081/1.082	1.079	1.082/1.082
$\alpha_{1/2}$	119.9	117.4	120.9	120.4	118.7	122.0	121.4/119.1	118.7	125.1/118.6
$\alpha_{3/6}$	122.7	126.3	120.8	121.9	123.7	118.9	121.7/122.6	123.8	118.9/120.1
$\alpha_{4/5}$	117.3	116.3	118.2	117.7	117.5	119.1	117.4/117.7	117.4	116.4/120.8
$\beta_{1/2}$	115.1	113.6	115.5	115.6	115.0	117.4	115.7/115.1	114.8	117.7/115.9
$\beta_{3/4}$	120.5	121.1	120.1	120.3	120.6	119.3	120.3/120.2	120.8	120.4/118.6

[a]Bond lengths in Angstroms and angles in degrees. See Figures for symbols:

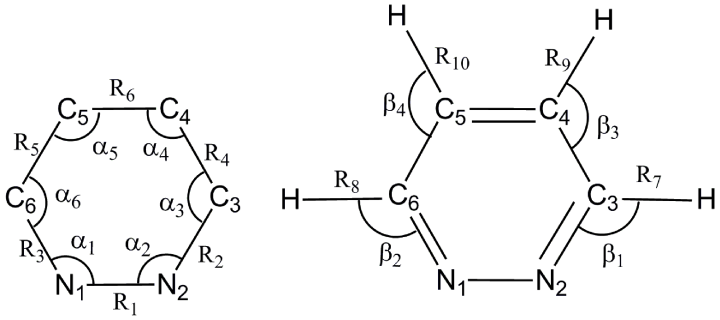


Table S6 Assignment of the M06-HF/LanL2DZ calculated wavenumbers of the Pdz-Ag_2 complex (C_{2v}) in the S_0;$^1A_1$, CT_0;$^1A_2$ and CT_1;$^1B_1$ electronic states.

Symmetry	Assignment[a]	S_0 ($^1A_1$) B3LYP/6-31+G*[b]	S_0 ($^1A_1$) M06-HF/LanL2DZ	CT_0 ($^1A_2$) M06-HF/LanL2DZ		CT_1 ($^1B_1$) M06-HF/LanL2DZ	
		ν/ cm^{-1}	ν/ cm^{-1}	ν/ cm^{-1}	D_{ij}[c]	ν/ cm^{-1}	D_{ij}[c]
A_1	2;ν(CH)	3120	3311	3330	-0.99	3298	-0.88
	7a;ν(CH)	3103	3286	3266	-0.99	3367	-0.88
	8a;ν_{ring}	1570	1689	1573	-0.82	1684	0.98
	19b;δ(CH)	1443	1507	1513	0.75	1447	0.99
	14;ν_{ring}	1167	1224	1333	-0.69	1413	0.80
	δ(CH)	1144	1209	1185	-0.74	1195	-0.83
	ν_{ring}	1064	1111	1015	-0.76	1081	0.84
	1;ν_{ring}	983	1016	920	-0.73	981	0.89
	6a;δ_{ring}	659	691	701	-0.98	647	1.00
B_2	20a;ν(CH)	3111	3296	3314	-0.93	3355	0.75
	13;ν(CH)	3095	3282	3263	0.93	3228	0.70
	8b;ν_{ring}	1565	1684	1541	0.68	4383	-0.88
	19a;δ(CH)	1404	1481	1405	-0.65	1417	0.96
	δ(CH)	1281	1348	1089	0.52	1329	-0.94
	ν_{ring}	1055	1119	1176	0.76	974	0.98
	12;δ_{ring}	1022	1072	1066	0.99	1073	1.00
	6b;δ_{ring}	612	639	582	-1.00	648	-0.99
A_2	5;γ(CH)	1006	1091	1044	-0.79	1038	0.91
	10b;γ(CH)	934	988	841	-0.79	668	-0.74
	4;τ_{ring}	753	798	689	-0.98	696	0.81
	16a;τ_{ring}	370	413	259	0.98	447	1.00
B_1	17b;γ(CH)	970	1039	1032	0.99	794	0.76
	11;γ(CH)	754	814	744	-0.96	664	-0.72
	16b;τ_{ring}	372	418	421	-0.98	133	0.70

[a]Wilson's nomenclature from G. Varsanyi, Vibrational spectra of benzene derivatives, Academic Press, New York, 1969. ν:stretching, δ:in-plane deformation, γ:out-of-plane deformation and τ:torsion. [b]B3LYP/6-31+G* wavenumbers for in-plane and out-of-plane fundamentals scaled by 0.97 and 0.99, respectively. [c]Biggest element of the Duschinski matrix.

Table S7 Vibrational wavenumbers (cm^{-1}) of the out-of-plane fundamentals of pyridazine (Pdz) in the $S_0;^1A_1$, $D_0;^2A_2$ and $D_1;^2B_1$ electronic states calculated at several levels of theory.

Electronic state:	S_0	S_0	D_0		D_1		S_0	D_0		D_1		S_0	D_0		D_1	
Method:	B3LYP	**B3LYP**	**UB3LYP**		**UB3LYP**		**RHF**	**UHF**		**UHF**		**CASSCF[a]**	**CASSCF[a]**		**CASSCF[a]**	
Basis set:	6-31+G*	**6-31+G***	**6-31+G***		**6-31+G***		**6-31+G***	**6-31+G***		**6-31+G***		**6-31+G***	**6-31+G***		**6-31+G***	
Asignment[b]	ν^c	ν	ν	D_{ij}^d	ν	D_{ij}^d	ν	ν	D_{ij}^d	ν	D_{ij}^d	ν	ν	D_{ij}^d	ν	D_{ij}^d
5,γ(CH),A_2	1006	1016	578	-0.73	885	-0.87	1141	677	0.67	1028	-0.88	1083	714	-0.68	977	0.91
17b,γ(CH),B_1	970	980	907	-0.94	443	0.80	1095	1030	-0.91	448	-0.72	1031	995	-0.92	516	0.76
10b,γ(CH),A_2	934	943	943	0.76	452	0.75	1048	1055	0.73	416	-0.89	984	1020	-0.71	512	-0.91
11,γ(CH),B_1	754	762	587	0.87	668	-0.85	850	667	0.80	774	-0.82	811	664	-0.91	746	-0.79
4,τ_{ring},A_2	753	761	664	0.93	666	-0.98	833	722	-0.89	727	-0.98	779	692	0.88	699	0.97
16b,τ_{ring},B_1	372	376	383	-0.92	298i	0.91	446	439	0.96	267i	0.76	440	440	-0.97	72i	0.86
16a,τ_{ring},A_2	370	374	211	0.99	411	-0.89	433	290	-0.92	487	-0.99	423	304	0.94	475	1.01

[a]6x6 and 7x6 CASSCF calculations for S_0 and D_i, respectively. [b]Wilson's nomenclature from G. Varsanyi, Vibrational spectra of benzene derivatives, Academic Press, New York, 1969. γ:out-of-plane deformation and τ:torsion. [c]Scaled B3LYP/6-31+G* wavenumbers by 0.99. [d]Biggest element of the Duschinski matrix.