Electronic Supplementary Material

Sensing atrazine herbicide degradation products through their interactions with humic substances by surface-enhanced Raman scattering

G. Zanasi[a], R. J. G. Rubira[b], O. Francioso[a], M. V. Cañamares[c],
C.J.L. Constantino[b], S. Sanchez-Cortes[c]

[a]Dipartimento di Scienze e Tecnologie Agro-Alimentari, V.le Fanin 40, 40127- Bologna, Italy

[b]São Paulo State University (UNESP), School of Technology and Applied Sciences, 19060-900, Presidente Prudente, SP, Brazil.

[c]Instituto de Estructura de la Materia, IEM-CSIC, Serrano 121, E-28006-Madrid, Spain

*Corresponding authors:
Rafael Jesus Gonçalves Rubira. São Paulo State University (UNESP), School of Technology and Applied Sciences, 19060-900, Presidente Prudente, SP, Brazil; rafael.gon.fis@gmail.com
Santiago Sanchez-Cortes, Instituto de Estructura de la Materia (IEM-CSIC), Serrano 121, E-28006-Madrid, Spain; s.sanchez.cortes@csic.es

Table S1. Assignments of this spectra DEHA keto and enolic form bands assignment. Note: calc.–calculated wavenumbers (cm^{-1}); expt.–experimental wavenumbers (cm^{-1}); δ_{ω}–wagging; ν–stretching; δ_{sc}–scissoring; ρ–rocking; δ_{tw}–twisting; δ–in plane deformation; ɣ–out-of-plane deformation; asymm.–asymmetrical; symm.–symmetrical; def.–deformation; bend.–bending.

Calc.		**Expt.**		**Assignment**
Raman		**Raman**	**SERS**	
Keto form	**Scaled**			
173.27	175.28	**173**		Skeletal vibration
198.27	200.58	**193**		Skeletal vibration
			210	Ag-O vibration
228.29	230.96	**219**		Skeletal vibration
241.70	244.52			Skeletal vibration
277.19	280.43			Skeletal vibration
313.73	319.28	**310**		δ_{ω} NH_2
351.46	355.57	**360**	**327**	δN-C-N
394.96	399.58			δC-C-C
425.26	430.23	**420**		ɣC-N-C
465.31	470.65	**448**	**448**	ƔN-H; ɣN-H
504.03	509.93			Ɣring; δN-C-C
536.82	543.10	**489**	**489**	δring; ɣN-H
539.42	545.73	**565**	**593**	ɣN-H
564.59	571.19	**578**		δ_{tw} NH_2; ɣN-H
578.43	585.20	**609**	**643**	δring; ɣN-H; δ_{tw} NH_2
612.96	620.13	**640**	**670**	ɣring; νC-N
			799	ɣring
819.03	828.61	**746**	**746**	symm. νCH-C-CH_3
935.06	946.00	**853**	**853**	νC-N; ρNH_2
936.56	947.52	**946**		ρCH; δC-H
948.86	959.96	**957**	**957**	asymm. νCH_3-C-CH_3; ρCH_3
977.99	995.30	**985**	**985**	νN-C-N; ρNH_2; νC-N; ρCH_3
1032.16	1044.24			ρNH_2; νN-C; νC-N; ρCH_3
1063.77	1076.22			ρNH_2; νC-N
1127.72	1088.02	**1095**	**1095**	ρNH_2; δC-C-C; ρCH_3
1146.70	1106.33	**1127**	**1127**	ρCH_3; asymm. νC-C-C
1183.09	1141.44	**1176**	**1168**	ρNH_2; ρCH_3; νring; νCN
1198.08	1155.90	**1203**		def. N-H; def. C-C-C; ρCH_3
			1222	def. C-N
1267.53	1222.91			νN-C; νN-C; ρCH_3
1321.89	1275.35	**1272**	**1272**	def. N-H; def. C-H; νC-C-C;bend. CH_3
1349.86	1302.34	**1307**	**1307**	def. C-H; νC-C-C; bend. CH_3

1386.46	1337.65	**1339**		def. C-H; vN-C-N
1403.34	1353.94			symm. def. CH_3
1404.22	1354.79			def. CH_3; def. C-H; def. N-H; vC-N-C
1425.91	1375.71	**1380**	**1371**	def. CH_3; def. C-H;
1486.87	1434.53			asymm. def. CH_3
1495.12	1442.49	**1441**	**1445**	asymm. def. CH_3
1503.70	1450.76	**1459**		asymm. def. CH_3
1506.16	1453.14	**1465**		asymm. def. CH_3; vN-C-N; def. N-H
1523.52	1469.89	**1469**		asymm. vCH_3; def. N-H; def. C-H
1549.69	1495.14	**1519**		vN-C-N; vN-C-N; def. N-H; def. C-H; δ_{sc} NH_2
1600.60	1544.26	**1558**	**1522**	δ_{sc} NH_2; def. N-H; def. N-H; vN-C-N; vN-C-N; vring
1647.36	1589.37	**1598**		δ_{sc} NH_2; def. N-H; vring; vN-C
1667.42	1608.42	**1627**		δ_{sc} NH_2; def. N-H; vN=C-N
1790.69	1701.15	**1669**	**1620**	vC=0; def. N-H; vC-N
3043.81	2891.62	**2882**	**2875**	symm. vCH_3
3052.29	2899.67	**2919**	**2919**	vC-H; symm vC-H_3
3110.96	2955.41	**2942**	**2936**	asymm. vCH_3
3114.24	2958.52			asymm. vCH_3
3141.33	2984.26	**2971**	**2971**	asymm. vCH_3
3144.74	2987.50	**2989**		asymm. vCH_3
3601.61	3421.51	**3052**		symm. VNH_2; vC-H
3616.11	3435.30	**3179**		vN-H
3639.74	3457.75	**3248**	**3353**	vN-H
3728.71	3542.27	**3507**		asymm. vNH_2

Calc.		**Expt.**		**Assignment**
Raman		**Raman**	**SERS**	

Enol form	Scaled			
177.16	179.23	**173**		Skeletal vibration
197.21	199.51	**193**		Skeletal vibration
			210	Ag-O vibration
206.32	208.73	**219**		Skeletal vibration
227.55	280.79			Skeletal vibration
241.33	244.15			Skeletal vibration
273.23	276.42			Skeletal vibration
352.89	357.02	**360**	**327**	def. C-N; def. O-C-N
391.42	395.99			def. CH_3-C-CH_3
424.24	429.20	**420**		ɣC-N-C
484.34	490.00	**448**	**448**	ɣN-H
507.21	513.14	**489**	**500**	δring; def. C-C-N
541.98	548.32	**565**	**593**	δring; δt_w NH_2
553.86	560.34			δt_w NH_2; ɣO-H
558.62	565.15	**578**		δt_w NH_2; ɣO-H
588.21	595.09	**609**	**643**	δring
629.15	636.51	**640**	**670**	ɣring; def. C-N-C
821.06	830.66	**746**	**746**	vCH_3-C-CH_3
			799	ɣring
821.25	830.85	**853**	**853**	vCH_3-C-CH_3
936.85	947.81			ρCH_3; def. C-H; vCH_3-C-CH_3
949.19	960.26	**957**	**957**	ρCH_3; def. C-H; vCH_3-C-CH_3
970.21	981.56	**985**	**985**	ρNH_2;vCH_3-C-CH_3; δring
988.60	1000.17			δring
1049.28	1061.56			ρNH_2; vCN; def. O-H
1101.06	1062.30			δring; vC-O; def. O-H; vC-N; def. C-N-C
1142.86	1102.63	**1095**	**1095**	ρCH_3; ρNH_2; δring; def C-O; def. O-H; def. C-N-C
1146.56	1106.20	**1127**		asymm. vCH-C-CH_3; ρCH_3
1187.00	1145.22			ρNH_2; ρCH_3; def. C-N-C; def. O-H
1215.91	1153.11	**1176**		def. O-H; vN-C; def. CH_3-C-CH_3
1261.82	1216.92	**1203**		def. O-H; vN-C
			1228	def. C-O; def. C=N
1306.44	1260.45	**1272**		def. O-H; def. N-H; ρNH_2; vring
1349.35	1301.85	**1307**		def. C-H; asymm. vCH_3-C-CH_3
1392.73	1343.70	**1339**		def. C-H; def N-H
1403.90	1354.48			asymm. vCH_3-C-CH_3; symm def. CH_3
1413.39	1363.64			def. N-H; def. O-H; symm. def. CH_3; vring

1427.77	1377.51	**1380**	**1371**	symm. def. CH_3; def. C-H; symm. νCH_3-C-CH_3; def. O-H; def. N-H
1478.91	1426.85			def. N-H; νring; def. O-H; νC-O; def. C-H
1486.51	1434.18			asymm. def. CH_3
1498.57	1445.8	**1441**	**1441**	asymm. def. CH_3; δsc NH_2; νC-N; def. N-H; def. C-H
1502.28	1449.40			δsc NH_2; asymm. def. CH_3; νC-N; νring; def. N-H
1504.40	1451.44	**1459**	**1459**	asymm. def. CH_3; νring
1522.29	1468.70	**1465**		asymm. def. CH_3
1583.51	1527.77	**1496**		δ_{sc} NH_2; νring; def. C-H; νC-N
1606.80	1550.24	**1558**	**1543**	δ_{sc} NH_2; def. C-H; νring; def. N-H; νC-N
1649.97	1591.89	**1598**	**1585**	δ_{sc} NH_2; νring; νC-N; def. O-H
1658.35	1575.43	**1627**		δ_{sc} NH_2; νring; νC-N; def. O-H; def. N-H
3043.23	2891.07	**2882**	**2875**	symm. νCH_3
3051.01	2898.46	**2919**	**2919**	symm. νC-H; symm νCH_3
3109.74	2954.25			asymm. νCH_3
3133.09	2957.43	**2942**	**2936**	asymm. νCH_3
3142.34	2985.23	**2971**	**2971**	asymm. νCH_3
3145.62	2988.33	**2989**		asymm. νCH_3
3628.26	3446.85	**3052**		symm. VNH_2; νC-H
3650.74	3468.20	**3248**		νN-H
3771.90	3583.30			asymm. νNH_2
3784.42	3595.20	**3507**		νO-H

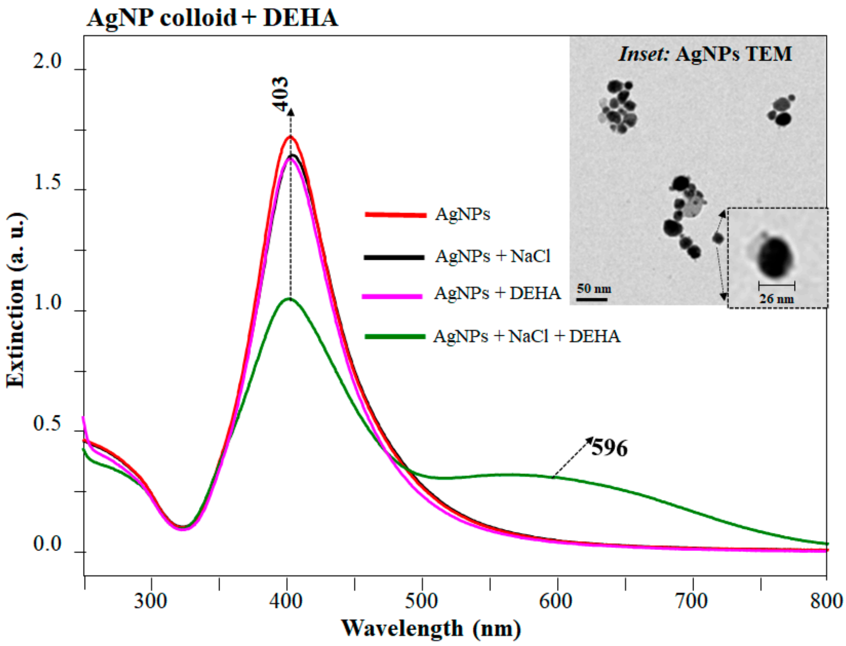
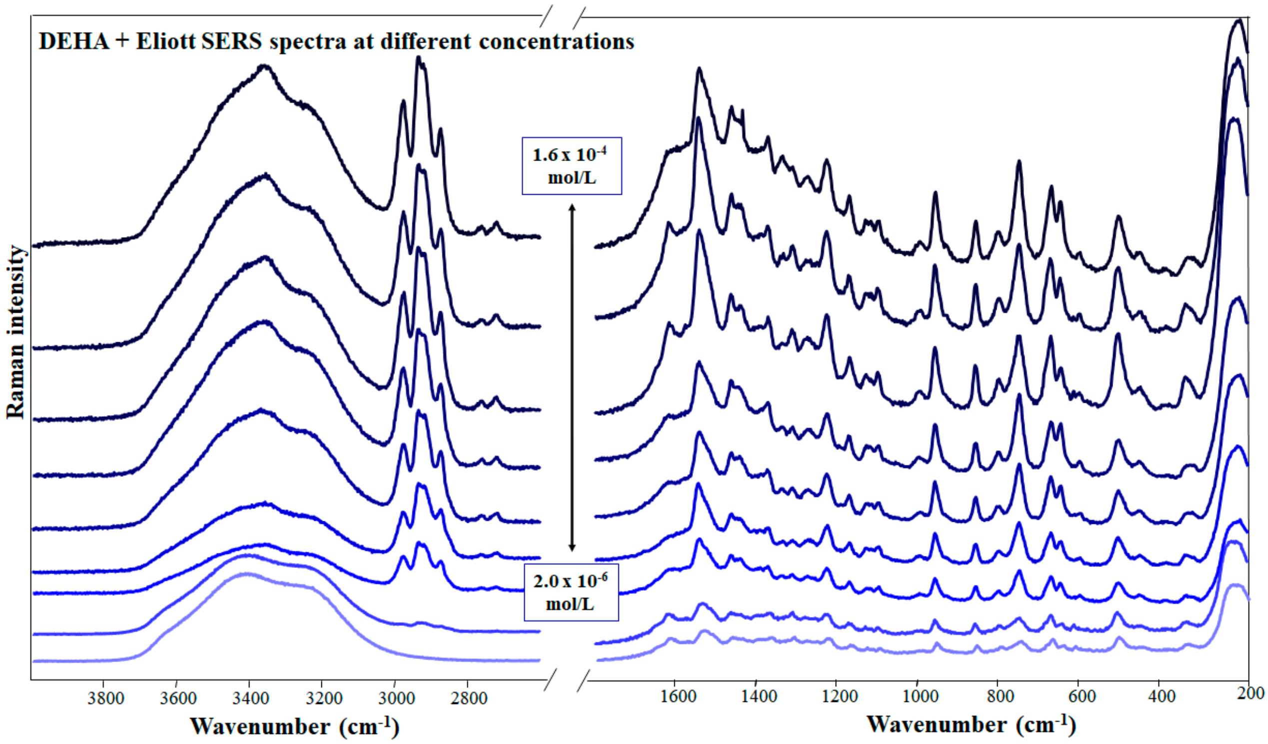


Figure S1: UV-Vis extinction spectra of the AgNPs in the absence and presence of NaCl salt (0.05 M) and DEHA (10^{-5} M). The insets show TEM image and diameter of AgNPs, respectively.



Figures S2: DEHA+Eliott soil SERS spectra at different concentrations of DEHA in AgHx colloid at pH 8.5. The concentration of the Eliott soil was kept constant to 1 mg/mL while changing the concentration of DEHA. The concentration of DEHA was varied from $2.0x10^{-6}$ to 1.6×10^{-4}. Laser line at 532 nm.

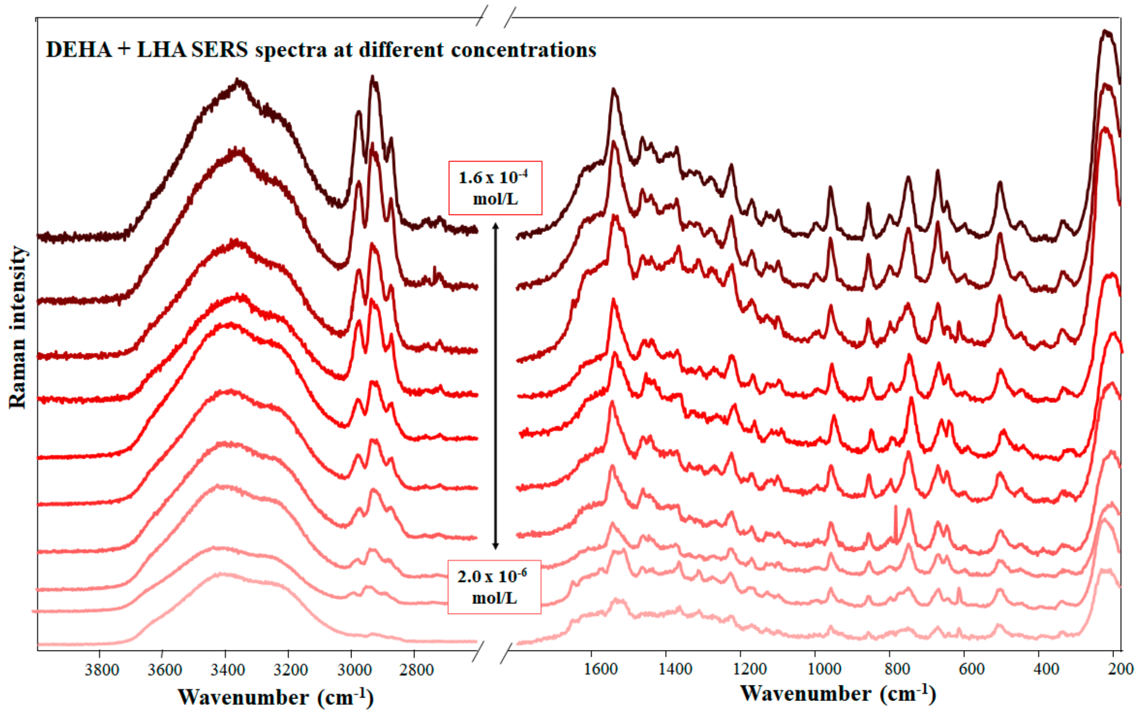


Figure S3: DEHA+LHA SERS spectra at different concentrations of DEHA in AgHx colloid at pH 8.5. The concentration of the Leonardite humic acid was kept constant to 1 mg/mL while changing the concentration of DEHA. The concentration of DEHA was varied from $2.0x10^{-6}$ to 1.6×10^{-4}. Laser line at 532 nm.

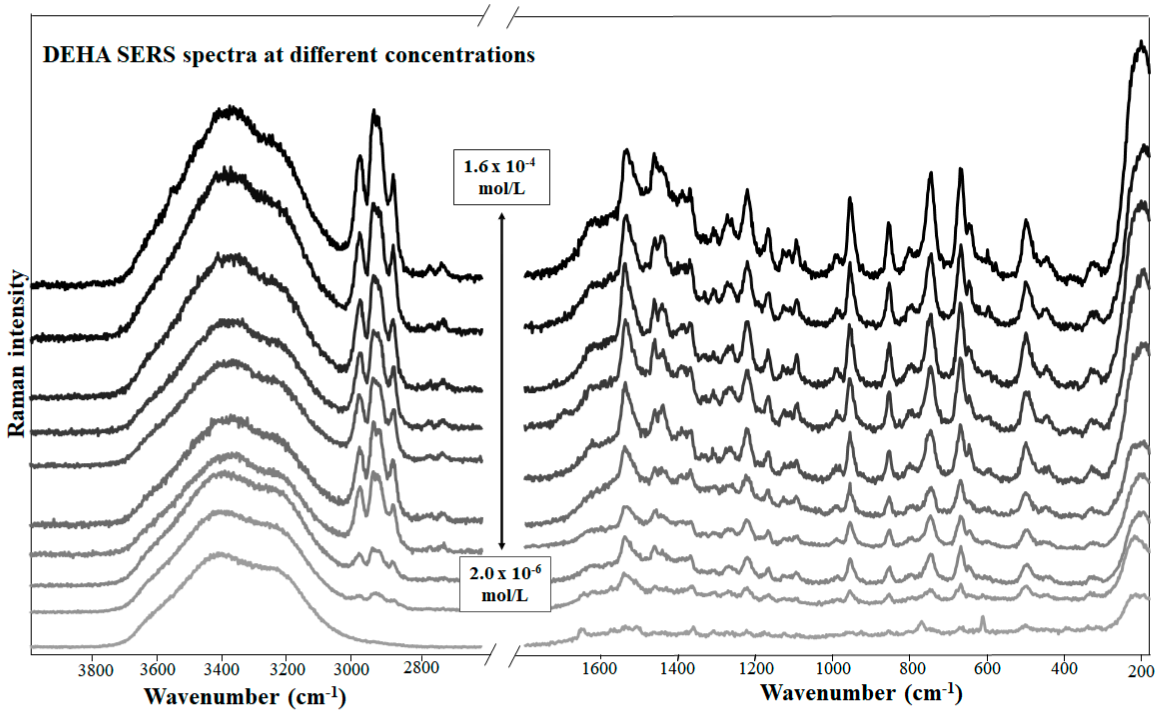


Figure S4: DEHA SERS spectra at different concentrations in AgHx colloid at pH 8.5. Final concentration of DEHA indicated in the figure; initial concentration of DEHA is from 2.0×10^{-6} to 1.6×10^{-4}. Laser line at 532 nm.