

Supporting Information

Highly Sensitive SERS Detection of Neonicotinoid Pesticides. Complete Raman Spectral Assignment of Clothianidin and Imidacloprid

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This supporting information document contains characterisation of the SERS sensor and detailed discussion of the vibrational analysis of Clothianidin and Imidacloprid

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S1. SERS sensor Characterisation with Crystal Violet

Figure S1 shows the SERS response of Crystal violet (a highly active SERS molecule) on the fabricated SERS sensors. All the characteristic peaks of crystal violet are well defined, indicating the presence of SERS hotspots on the surface.

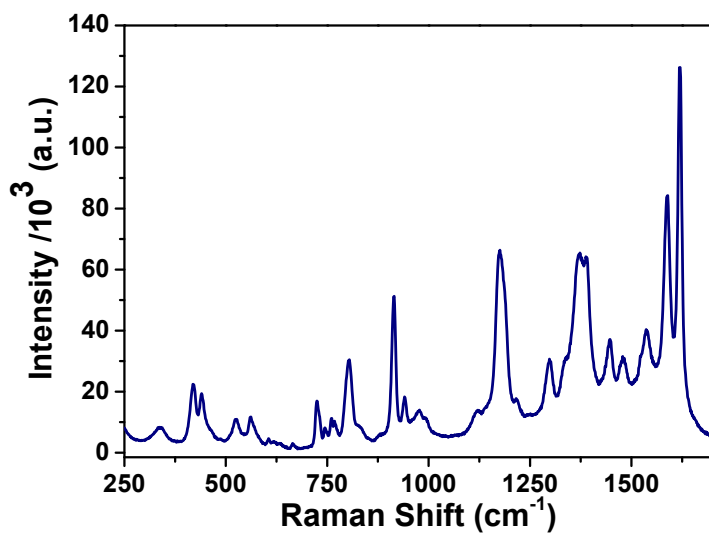


Figure S1: SERS spectrum of 10^{-6} M crystal violet in water

S2. Clothianidin Vibrational Analysis

Raman	SERS (1ng)	DFT (sim)	DFT (scaled)	Vibrational Assignments
3086	-	3622.54	3502.63	N6-C20 stretch
3013	-	3594.94	3475.94	N5-C18 stretch
2983	-	3228.15	3121.3	C13-C19 stretch
2952	-	3114.61	3011.52	C10-H16, H17 as stretch
2936	-	3099.38	2996.8	C15-C22 stretch
	-	3067.09	2965.57	C10-H16, H17 sym stretch
	-	2999.81	2900.52	C15-C23, 24 as stretch
	-	2957.86	2859.95	C15-C22, C23, 24 sym stretch

Table S1: Vibrational assignments of the CH modes at the upper end of the clothianidin Raman spectrum

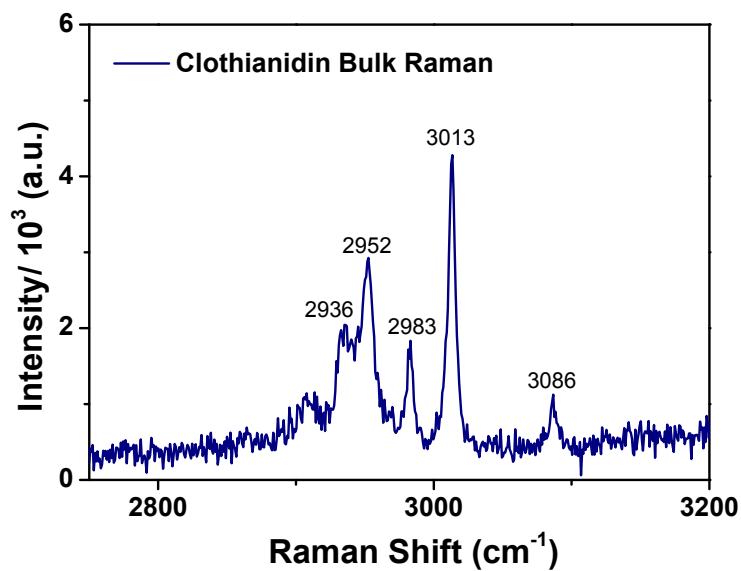


Figure S2: Raman spectrum for Clothianidin bulk powder at the higher wavenumber range.

C-H vibrations

From DFT calculations, all CH vibrations in the molecule were assigned to their corresponding Raman band using the vibrations illustrated in the simulation. First the ring C13-H is discussed followed by the C10-H vibrations and finally the C15-H vibrations. All the single C-H stretching vibrations observed at an extended spectral range ($\sim 3000 - 3600 \text{ cm}^{-1}$) were assigned and are presented in Table S1 (Supp Info). The Raman band at 3121 cm^{-1} was assigned as the only stretching vibration for the CH bond in the chlorothiazole ring, C13-H19. There are, however, several in-plane bending vibrations associated with C13-H, which were observed at 1532 cm^{-1} , 1296 cm^{-1} , 1248 cm^{-1} and 1152 cm^{-1} . The first mode was strongly coupled with C13-C11, C10 and N7-C14 stretching vibrations. The second and third were coupled with a C10-H twisting vibration, whereas the last mode was coupled with a C10-H rocking. The out of plane wagging modes for C13-H are observed at 871 cm^{-1} and 669 cm^{-1} . The C10-H symmetric and asymmetric stretching modes are observed at 2965 cm^{-1} and 3011 cm^{-1} , respectively. The only C10H bending vibration was assigned at 1462 cm^{-1} . Alternatively, multiple out of plane twisting modes were found at 1422 cm^{-1} , 1296 cm^{-1} , 1248 cm^{-1} and 1051 cm^{-1} ; including a C10H16 out of plane wagging at 1318 cm^{-1} . Finally Raman bands at 1152 cm^{-1} , 947 cm^{-1} , 669 cm^{-1} and 259 cm^{-1} can be assigned to the in-plane rocking of H16 and H17 with C10. The C15-H symmetric and asymmetric stretching modes are observed at 2860 cm^{-1} and 2900 cm^{-1} , respectively. Raman peaks at 1422 cm^{-1} and 992 cm^{-1} were assigned to the in-plane bending and wagging modes of the CH_3 bonds, respectively.

Ring Vibrations

Stretching Raman vibrations were assigned, followed by the in-plane bending and out-of-plane wagging modes, and finally the C-Cl bond vibrations are discussed. Strong ring C13-C11 and N7-C14 stretching modes are observed at 1532 cm^{-1} and 1433 cm^{-1} in the Raman spectrum, and are both coupled with a C10-C11 stretch. The C13-N7 stretching vibration is observed at 1152 cm^{-1} in Raman spectra. This band is also coupled with a C10-C11 stretch, as well as a C11-S2 stretch. A strong asymmetric stretch between C14-S2, Cl1 observed at the simulated value of 1029 cm^{-1} , was assigned to the 992 cm^{-1} band in the Raman spectrum, and coupled with a N7-C14 bending mode. Weak S2-C13, C11 symmetric and asymmetric stretching vibrations are observed at 651 cm^{-1} and 669 cm^{-1} , respectively. The former is coupled with C12N5C10H wagging out of plane vibrational mode. The observed band at 594 cm^{-1} in Raman spectrum is assigned to the out of plane wagging modes of the chlorothiazole ring, where C13 and C14 are vibrating out of plane in an opposite direction to N7. The other out-of-plane wagging modes were observed at 443 cm^{-1} and 358 cm^{-1} . The vibrational modes for the C-Cl bond appeared at lower wavenumbers. The

stretching vibration of C14-Cl1 was seen at 443 cm^{-1} in the Raman spectrum (432.6 cm^{-1} in the SERS), this is agreement with the literature data.² Raman peaks at 259 cm^{-1} and 358 cm^{-1} can be assigned to the weak bending and wagging mode of C-Cl, respectively. Both vibrations are strongly coupled with a C10-H rocking.

N-O, N-H and C-N Vibrations

The N9-O symmetric and asymmetric stretching vibrations occur at 1318 cm^{-1} and 1570 cm^{-1} , respectively. The former, at 1318 cm^{-1} is coupled with weak stretching modes for N9-N6 and C12-N6, whereas the latter is coupled with the N-H bending of N6 and N5. These are two well resolved bands in both the Raman and SERS spectra, which compare well to the nitroalkane stretching reported in the literature.^{2,3} The wagging out of plane vibration of N9-O appears as the only observed band at 754 cm^{-1} ; while the N9-O rocking occurs at 358 cm^{-1} , which is coupled with C12N6N9 bending in plane. The strong N9-N6 stretching appears at 992 cm^{-1} . The C12-N6 stretching mode is observed at 1152 cm^{-1} . The C12-N wagging vibrations occur at 669 cm^{-1} with C12 vibrating out of plane in opposite directions to the nitrogen atoms. Finally the C-N bending mode for this carbon is observed at 1318 cm^{-1} . Another C-N vibration witnessed was the N8-C15 stretching bands at 651 cm^{-1} , 947 cm^{-1} and 1051 cm^{-1} which are coupled with a strong in plane N5-C10, C12 bending; a N5-H bend and a N5-C10 stretch, respectively. The Raman band at 310 cm^{-1} shows the bending vibration from N5 through C12 to O4 (N5C12N6N9O4) and simultaneously a bending from N6 through to C15 (N6C12N8C15H). This band also reveals a N5-H18 wagging vibration. Similar bending and wagging vibrations are also seen at 443 cm^{-1} . The out of plane N-H wagging vibrations (N6H20 and N5H18) are observed at 651 cm^{-1} , 514 cm^{-1} and 577 cm^{-1} . The latter band is coupled with a weak ring wagging vibration (C11S2C14), where C11 and C14 are vibrating out of plane. The in-plane N-H bending modes are observed at several higher wavenumbers; 1051 , 1248 , 1318 , 1422 , 1532 cm^{-1} .

S3. Imidacloprid Vibrational Analysis

Raman	SERS (1ng)	DFT (sim)	DFT (scaled)	Vibrational Assignments
	-	3570.49	3452.3	N6-C24 stretch
	-	3216.04	3109.6	C13,14 - H25,27 sym stretch
	-	3198.71	3092.83	C13,14 - H25,27 as stretch
3051	-	3147.86	3043.66	C15-C26 stretch
2988	-	3111.06	3008.08	C10-H21 stretch
2970	-	3094.97	2992.53	C9-H19, C11-H23 as stretch
2951	-	3084.63	2982.53	C9-H19, C11-H23 sym stretch
2930	-	3034.32	2933.884	C11-H22 stretch
2900		2982.76	2884.03	C9-H18 stretch
		2976.43	2877.91	C10-H20 stretch

Table S2: Vibrational assignments of the C-H modes at the upper end of the imidacloprid Raman spectrum

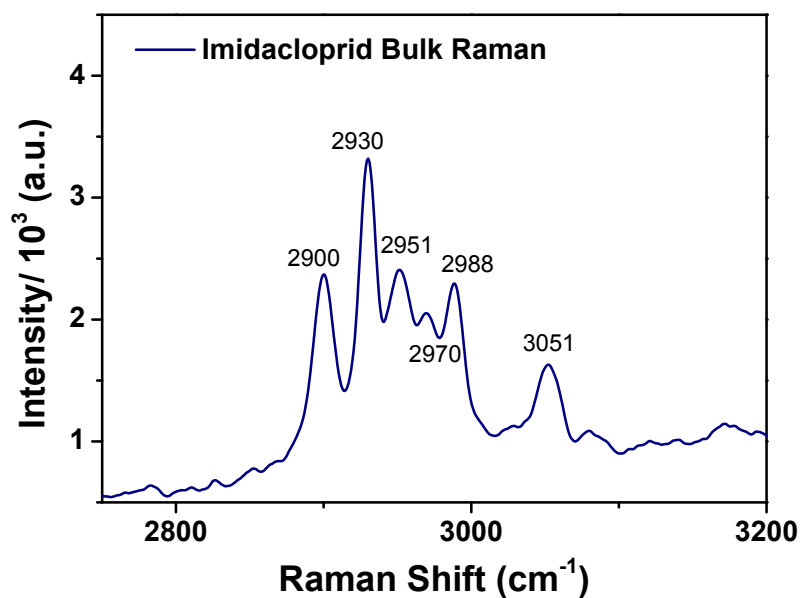


Figure S3: Raman spectrum for Clothianidin bulk powder at the higher wavenumber range.

C-H vibrations

There are 3 C-H bonds in the chloropyridine ring structure; C14, C15 and C16. Their stretching modes all vibrate as frequencies above $\sim 3000\text{ cm}^{-1}$, which is typical for C-H hetero-aromatic stretching vibrations.⁴ These peaks are illustrated in the Raman spectrum of the extended spectral range for imidacloprid, in Figure S4. All these C-H stretching vibrations were assigned and are presented in at the beginning of Table S2. There are several in-plane vibrations associated with the ring CH structures. The bending vibrations for C14H, C15H and C16H are observed at 1451 cm^{-1} , 1371 cm^{-1} and 1277 cm^{-1} , which were all coupled with stretching vibrations associated with Ring 1. Another band at 1109 cm^{-1} demonstrated the strong in-plane bending between the two hydrogens associated with C14 and C16 (H25 and H27). This band was also coupled with a C14-C16 stretching. The out of plane wagging modes for the pyridine ring C-H bonds are observed at 1142 cm^{-1} and coupled with a strong C13-C10 stretching mode.

The vibrational frequencies corresponding to C9H and C11H of ring 2 are also presents in Table S2 (Supp. Info). Briefly, the Raman bands observed at 2951 cm^{-1} and 2970 cm^{-1} are assigned to C9H and C11H symmetric and asymmetric stretching modes, respectively. The strong in plane bending vibration for C9-H and C11-H appears as the only observed band at 1484 cm^{-1} . No other C9H or C11H bending modes were seen in the simulated vibrations. The wagging out of plane vibrational mode of C9-H and C11-H was assigned as 1302 cm^{-1} in Raman spectra and was coupled with a C9-C11 weak stretching vibration. The other out of plane wagging modes were observed at 1277 cm^{-1} and 1241 cm^{-1} . The former band was coupled with CH bending vibrations in ring 1; and the latter band was strongly coupled with ring 1 stretching vibrations and weak asymmetric stretching in ring 2. The only twisting vibration for the C9-H and C11-H bonds was observed at 1195 cm^{-1} . Finally multiple C9-H and C11-H in-plane rocking modes were observed at 815 cm^{-1} , 751 cm^{-1} , 691 cm^{-1} and 142 cm^{-1} . The first was coupled with a C10-C13 stretching mode and the oth

er three bands were coupled with a C10-C13, N4 bending vibration.

The C10 symmetric stretching modes with H21 and H20 were observed at 3008 cm^{-1} and 2878 cm^{-1} , respectively in the simulated data. The only C10H bending vibration was assigned at 1451 cm^{-1} in the Raman spectrum. Multiple out of plane vibrational modes were observed for the C10-H20, H21 bonds in the Raman spectrum; including twisting vibrations at 1277 cm^{-1} and 1241 cm^{-1} , and wagging vibrations at 1371 cm^{-1} , 1302 cm^{-1} and 1142 cm^{-1} . Finally Raman band at 282 cm^{-1} was assigned to the in-plane rocking of H20 and H21 with C10.

Ring Vibrations

The vibrations for Ring 1 (chloropyridine) are studied first followed by the vibrations for ring 2 (imidazole). The 1568 cm^{-1} is one of the dominating Raman peaks and can be attributed to the pyridine ring stretching mode. In particular, this band represents the asymmetric stretching between C13 and C17 with their adjoining atoms (vC13C14C15 and vC17N8C16). Similarly, the band at 1451 cm^{-1} represents a C16-C17, C14 asymmetric stretching vibration and is coupled with a very weak C17-N8 stretch. A weak symmetric stretching at 1371 cm^{-1} was observed for C16 and C15 and their respective bonded atoms. The other ring stretching modes were observed at 1142 cm^{-1} and 815 cm^{-1} . The first band could be recognized as a ring breathing mode, but mainly consisted of an in-plane ring stretching from C13 to C14 and C15, with an asymmetric stretch to the out-of-ring C10. The second ring vibrations at 815 cm^{-1} contained a symmetric stretch from C13 to C14, C15 and C10; and a C17 ring bending with C16 and N8 which was coupled with a C17-C11 stretch. Some weak ring bending vibrations were observed at and 998 cm^{-1} and 691 cm^{-1} . The former band contains two bending modes C17-C16, N8, and C13- C14, C15, where by the C17 and C13 atoms are stationary. On the other hand, the latter band contains a C13-C14, C15 bend, whereby all the other ring atoms are vibrating with the bending mode, including a C17-C11 stretch. There is also weak ring vibration at 660 cm^{-1} consisting of a C13 bend with C14 and C15 coupled with a C17-C11 stretch and C10 bending with C13 and N4. Finally, the Raman peak at 631 cm^{-1} exhibited the strongest bending vibrations for the pyridine ring, specifically, the symmetric bending of C14 with C13/ C16 and N8 with C15/ C17 which was coupled with a weak ring 2 bending vibration, C9-N4, C11. The Raman band at 476 cm^{-1} attributed to the only out of plane wagging of the pyridine ring, in particular, the C13 and C17 atoms are vibrating in the opposite direction to the other 4 atoms in the ring. This band is coupled with a C17C11 stretching and the bending of C10 with C13 and N4.

Raman vibrations associated with the C9 and C11 atoms of ring 2 were mostly discussed in the above “CH vibrations” section. Subsequently we assigned the remaining ring modes and also included vibrations involving the C12 carbon and its surrounding 3 nitrogen atoms. The C9-C11 stretching is observed at 982 cm^{-1} , in the simulated data. Due to the orientation of imidacloprid the majority of the imidazole ring modes were observed as out-of plane vibrations. However in-plane rocking and breathing modes were observed at 475 cm^{-1} and 751 cm^{-1} , respectively. The former involved rocking of the entire ring, in-plane, across the C10-N4-C12-N6 bond, while the atoms C10 and N6 remained stationary. The Raman band at 320 cm^{-1} was assigned as a ring wagging, mainly involving vibration of the N4-C12-N5 bond out-of-plane. A strong C12-N asymmetric stretching was observed at 1584 cm^{-1} in the Raman spectrum, which is one of the characteristic peaks for imidacloprid (1607 cm^{-1} in the SERS spectrum). A second weaker asymmetric

stretching was seen at 1241 cm^{-1} . The common C12-N wagging vibrations were observed at 691 cm^{-1} and 660 cm^{-1} , whereby the C12 vibrated out-of-plane in opposite directions to the three surrounding nitrogen atoms. The latter band was coupled with the bending of C9 with N4 and C11.

N-O and C-N Vibrations

In this section, all the peaks associated with the nitro-structure were assigned; first the N7-O2, O3 modes were investigated, followed by the vibrations between N6-N7, and finally the N-H bond was studied. The N7-O symmetric and asymmetric stretching vibrations occur at 1302 cm^{-1} and 1584 cm^{-1} , respectively. The former is coupled with a weak N6-N7 stretch and the latter is coupled with the strong N6-H24 bending mode. These are two well resolved bands in both the Raman and SERS spectra, which compare well to the nitroalkane stretching reported in the literature.⁴ A weak symmetric N-O stretching was also found at 1277 cm^{-1} . The out of plane wagging vibration of N7-O is observed at 751 cm^{-1} ; while the bending vibration of N6N7O2O3 occurs at 142 cm^{-1} .

The N6-N7 stretching was observed at 1241 cm^{-1} in the Raman spectrum, with a second strong stretching vibration revealed at $\sim 1050 \text{ cm}^{-1}$ in the simulated data. A strong in-plane N6N7O2 bending mode was also observed at 443 cm^{-1} in the simulated data. The stretching vibration for N6-H24 was observed as highest mode in the simulated data, at 3452 cm^{-1} . The out of plane N-H wagging vibration for N6-H24 was observed at 631 cm^{-1} and a similar out of plane wagging vibration with N6-C12,H24 was identified at 691 cm^{-1} .

References

1. K. Dawson, M. Baudequin, N. Sassi, A. J. Quinn and A. O'Riordan, *Electrochimica Acta*, 2013, **101**, 169-176.
2. G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, John Wiley & Sons, 2001.
3. X.-M. Zhu, S.-Q. Zhang, X. Zheng and D. L. Phillips, *The Journal of Physical Chemistry A*, 2005, **109**, 3086-3093.
4. D. Lin-Vien, N. B. Colthup, W. G. Fateley and J. G. Grasselli, *The handbook of infrared and Raman characteristic frequencies of organic molecules*, Elsevier, 1991.