

## Supplementary information on:

# Multiscale description of molecular adsorption on gold nanoparticles by nonlinear optical spectroscopy

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### *Density Functional Theory methodology*

All DFT calculations were performed with hybrid functionals B3LYP and PBE0, using the Gaussian 09 package [S1]. Geometries were optimised under a convergence criterion of  $10^{-5}$  atomic units for RMS forces. Basis set 6-311++G(d,p) was used for light atoms (H, C and S). The gold atom was described by the Stuttgart-Dresden effective core potential for 1s-4f electrons and gaussian basis set for the valence electrons (19 valence electrons were considered), to which a f-shell polarization gaussian function was added, following the method described in [S2]. The results were comparable to those obtained with a more complete basis [S3] at lower computational cost. It was checked that additional d-shell and p-shell polarization functions had no major effect on the calculations. The choice of functionals, basis sets and effective core potentials is coherent with the literature for organic molecules and vibrational analysis involving 5d metals [S4]. Vibration modes, infrared and Raman activities were calculated using the standard software procedures. Thiophenol having no electronic transition in the visible range probed by SFG, static Raman polarizability calculations were performed. Tests to compare the results to dynamic polarizability calculations have confirmed that they showed no quantitative improvement on the Raman intensities. In a second step, anharmonicity [S5] was taken into account in order to improve the calculated frequencies through the appropriate option of the Gaussian 09 package. The perturbative anharmonic calculation was limited to the four vibration modes under study. Visualization of geometries and vibration modes was done using the Gabedit software [S6].

The results described in the Main text are displayed in the following tables. Columns outlined in bold contain data used in Table 5 of the Main text. Frequencies are in  $\text{cm}^{-1}$ , IR intensities in  $\text{km.mol}^{-1}$  and Raman scattering activities in  $\text{\AA}^4/\text{amu}$ , where amu stands for atomic mass unit.

B3LYP functional

	Thiophenol planar	Thiophenol perp.	GBT planar	GBT perp.
SCF (Ha)	-630.525362	-630.524332	-765.711168	-765.714978
$\Delta E / T_{eq.}$	28.03 meV / 52.6K		103.7 meV / 930K	
Mode 1 (harm.)	1014.0482	1016.7799	1009.2808	1015.1127
Anharmonic	1005.175	1014.652	1008.033	1003.151
IR	0.5236	1.8049	1.4339	2.2725
Raman	46.9893	39.1986	78.3691	75.7779
Mode 2 (harm.)	1044.9578	1043.2688	1043.0395	1041.1260
Anharmonic	1025.831	1026.566	1024.926	1022.090
IR	12.7688	10.8786	22.6502	2.8881
Raman	23.0352	16.2642	42.8627	120.6724
Mode 3 (harm.)	1104.2913	1093.8982	1099.5395	1094.0985
Anharmonic	1074.639	1069.553	1072.092	1068.632
IR	5.9066	4.3843	6.3535	4.6369
Raman	3.7709	0.2142	0.7001	0.0773
Mode 4 (harm.)	1111.2678	1104.6781	1094.2258	1089.9396
Anharmonic	1091.004	1082.637	1069.000	1063.509
IR	29.5672	3.0707	27.5052	9.1167
Raman	16.2758	8.7381	52.3838	386.1574

PBE0 functional (frequencies in Table 5 are scaled by 0.992)

	Thiophenol planar	Thiophenol perp.	GBT planar	GBT perp.
SCF (Ha)	-630.082342	-630.081144	-765.217762	-765.220688
$\Delta E / T_{eq.}$	32.6 meV / 105.2K		79.6 meV / 650.8K	
Mode 1 (harm.)	1016.2952	1018.6013	1011.7512	1017.4046
Anharmonic	1005.600	1016.629	1010.172	1006.018
IR	1.9924	3.8418	3.6415	2.5682
Raman	31.5533	26.4009	51.7138	29.4714
Mode 2 (harm.)	1056.7111	1054.2403	1055.7401	1052.6066
Anharmonic	1037.880	1036.616	1036.060	1033.175
IR	10.5776	8.3283	18.1043	3.4875
Raman	31.4486	24.6315	51.3527	106.1931
Mode 3 (harm.)	1111.8571	1100.5907	1106.7817	1100.3283
Anharmonic	1080.607	1076.878	1075.303	1075.588
IR	4.5650	5.4344	7.4571	5.9249
Raman	1.7006	0.2329	0.1604	0.0857
Mode 4 (harm.)	1131.7079	1124.2699	1116.0150	1110.6807
Anharmonic	1108.536	1099.633	1092.475	1083.754
IR	30.8117	2.3554	28.8258	5.4355
Raman	26.1692	13.7731	68.9464	388.4918

Comparison of the calculated frequencies (free molecule) without any correction factor

Mode	Literature	Harmonic B3LYP	Ratio	Anharmonic B3LYP	Ratio	Harmonic PBE0	Ratio	Anharmonic PBE0	Ratio
1	1002	1014.048	0.988	1005.175	0.997	1016.295	0.986	1005.600	0.996
2	1026	1044.958	0.982	1025.831	1.000	1056.711	0.971	1037.880	0.988
3	1072	1104.291	0.971	1074.639	0.998	1111.857	0.964	1080.607	0.992
4	1093	1111.268	0.984	1091.004	1.002	1131.708	0.966	1108.536	0.985
$\sigma$			$7.27e^{-3}$		$2.22e^{-3}$		$9.95e^{-3}$		$4.79e^{-3}$

Taking into account anharmonicity allows to reduce the span of the correction factors and shift it much closer to unity. Ratios are defined by theoretical values over experimental ones and measure the correction factor. All values are in  $\text{cm}^{-1}$ ,  $\sigma$  stands for the standard deviation.

Comparison of the calculated frequencies (GBT) without any correction factor

Mode	Literature	Harmonic B3LYP	Ratio	Anharmonic B3LYP	Ratio	Harmonic PBE0	Ratio	Anharmonic PBE0	Ratio
1	1000	1015.113	0.985	1003.151	0.997	1017.405	0.983	1006.018	0.994
2	1025	1041.126	0.985	1022.090	1.003	1052.607	0.974	1033.175	0.992
3	1065	1094.099	0.973	1068.632	0.997	1100.328	0.968	1075.588	0.990
4	1075	1089.940	0.986	1063.509	1.011	1110.681	0.968	1083.754	0.992
$\sigma$			$6.18\text{e}^{-3}$		$6.63\text{e}^{-3}$		$7.09\text{e}^{-3}$		$1.63\text{e}^{-3}$

The same conclusions as above can be drawn, except that B3LYP is unable to account for the correct mode assignment, even with anharmonic correction.

References

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