Supporting Information

The adsorption of nitrobenzene over alumina-supported palladium: an infrared spectroscopic study

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Figure S1.   Diagram of nitrobenzene with respect to a specified xyz-coordinate (blue = nitrogen; red = oxygen), with the z axis defining the principal component axis of the molecule.

Figure S2. Form of the vibrational modes for a mono-substituted benzene in C_{2v} symmetry as calculated by DFT (B3LYP/aug-cc-pVDZ), labelled using the Gardner and Wright notation. Reproduced from reference [38] with permission of the American Institute of Physics.

Table S1.   Approximate wavenumber ranges for the $\mathcal{M}$i vibrations. Adapted from reference [38] with permission of the American Institute of Physics.

Mode number ($\mathcal{M}$)	Symmetry	Wavenumber range / cm^{-1}
1	A_1	3060–3100
2	A_1	3040–3090
3	A_1	3000–3060
4	A_1	1570–1610
5	A_1	1460–1510
6	A_1	1050–1300
7	A_1	1140–1180
8	A_1	1010–1040
9	A_1	990–1010
10	A_1	640–820
11	A_1	240–530
12	A_2	950–980
13	A_2	810–860
14	A_2	400–420
15	B_1	960–1000
16	B_1	870–940
17	B_1	710–800
18	B_1	670–700
19	B_1	410–550
20	B_1	160–250
21	B_2	3030–3100
22	B_2	3020–3070
23	B_2	1570–1590
24	B_2	1410–1470
25	B_2	1310–1340
26	B_2	1250–1300
27	B_2	1120–1180
28	B_2	1060–1090
29	B_2	610–630
30	B_2	150–410

Table S2. Vibrational transition energies, infrared intensities, and assignments for nitrobenzene in the solid state as calculated by periodic-DFT.

Freq[a] / cm^{-1}	Symm[b]	Infrared intensity / (D/Å)^2 amu^{-1}	Infrared active?	Raman active?	Ave[c] / cm^{-1}	Range[d] / cm^{-1}	Assignment[e]
0	Bu	0.000	N	N	24	53	Acoustic translation
0	Bu	0.000	N	N	36	60	Acoustic translation
0	Au	0.000	N	N			Acoustic translation
30	Au	0.006	Y	N			Translation
41	Ag	0.000	N	Y			Translation
43	Bu	0.009	Y	N	68	35	Translation
47	Bg	0.000	N	Y	54	11	Libration
52	Au	0.010	Y	N			Libration
53	Bg	0.000	N	Y			Translation
53	Ag	0.000	N	Y			Translation
58	Bu	0.560	Y	N			Libration
58	Ag	0.000	N	Y			Libration
60	Bg	0.000	N	Y			Translation
65	Au	0.025	Y	N	77	27	Libration
73	Ag	0.000	N	Y			Translation
75	Bg	0.000	N	Y			Libration
77	Bu	0.135	Y	N			Libration
77	Au	0.001	Y	N			Translation
77	Bg	0.000	N	Y			Translation
82	Au	0.330	Y	N	91	23	Libration
83	Bu	0.255	Y	N			Libration
85	Ag	0.000	N	Y	94	17	Ph-NO$_2$ torsion
89	Au	0.023	Y	N			Ph-NO$_2$ torsion
92	Ag	0.000	N	Y			Libration
93	Bg	0.000	N	Y			Libration
99	Bu	0.013	Y	N			Ph-NO$_2$ torsion
103	Bg	0.000	N	Y			Ph-NO$_2$ torsion
105	Ag	0.000	N	Y			Libration
188	Au	0.019	Y	N	198	20	$\mathcal{M}$20
190	Bu	0.249	Y	N			
207	Bg	0.000	N	Y			
207	Ag	0.000	N	Y			
250	Au	0.162	Y	N	252	5	$\mathcal{M}$30
251	Ag	0.000	N	Y			
252	Bg	0.000	N	Y			
255	Bu	0.098	Y	N			
388	Au	0.138	Y	N	389	4	$\mathcal{M}$11
389	Bg	0.000	N	Y			
390	Bu	0.118	Y	N			
391	Ag	0.000	N	Y			
396	Bu	0.004	Y	N	403	14	$\mathcal{M}$14
401	Ag	0.000	N	Y			
404	Au	0.014	Y	N			
410	Bg	0.000	N	Y			

432	Ag	0.000	N	Y	433	4	$\mathcal{M}$19
432	Bu	0.179	Y	N			
433	Au	0.003	Y	N			
436	Bg	0.000	N	Y			
518	Bg	0.000	N	Y	519	2	NO_2 rock ($\mathcal{M}$30)
518	Ag	0.000	N	Y			
519	Bu	0.440	Y	N			
520	Au	0.318	Y	N			
601	Au	0.000	Y	N	603	4	$\mathcal{M}$29
602	Bg	0.000	N	Y			
604	Bu	0.042	Y	N			
605	Ag	0.000	N	Y			
673	Bu	4.637	Y	N	675	3	$\mathcal{M}$18
673	Au	0.582	Y	N			
676	Bg	0.000	N	Y			
676	Ag	0.000	N	Y			
678	Au	0.606	Y	N	679	2	$\mathcal{M}$10
678	Bg	0.000	N	Y			
679	Bu	0.227	Y	N			
680	Ag	0.000	N	Y			
698	Bu	8.052	Y	N	704	11	$\mathcal{M}$17
705	Au	2.887	Y	N			
706	Ag	0.000	N	Y			
709	Bg	0.000	N	Y			
794	Au	0.830	Y	N	797	6	NO_2 wag
796	Bu	0.789	Y	N			
799	Ag	0.000	N	Y			
800	Bg	0.000	N	Y			
815	Au	0.156	Y	N	825	17	$\mathcal{M}$13
823	Bg	0.000	N	Y			
827	Bu	0.130	Y	N			
833	Ag	0.000	N	Y			
848	Au	1.716	Y	N	849	2	NO_2 scissors
849	Ag	0.000	N	Y			
849	Bu	1.706	Y	N			
850	Bg	0.000	N	Y			
931	Au	0.058	Y	N	936	11	$\mathcal{M}$16
933	Bu	0.693	Y	N			
941	Bg	0.000	N	Y			
941	Ag	0.000	N	Y			
964	Bu	0.137	Y	N	971	13	$\mathcal{M}$12
971	Ag	0.000	N	Y			
972	Au	0.102	Y	N			
977	Bg	0.000	N	Y			
992	Ag	0.000	N	Y	994	4	$\mathcal{M}$9
993	Bu	0.379	Y	N			
994	Bg	0.000	N	Y			
996	Bg	0.000	N	Y			
996	Au	0.038	Y	N	1000	7	$\mathcal{M}$15
1000	Ag	0.000	N	Y			

1000	Au	0.215	Y	N			
1003	Bu	0.015	Y	N			
1014	Ag	0.000	N	Y	1016	4	$\mathcal{M}8$
1015	Bu	0.300	Y	N			
1017	Bg	0.000	N	Y			
1018	Au	0.118	Y	N			
1071	Bu	0.918	Y	N	1073	6	$\mathcal{M}28$
1073	Au	3.308	Y	N			
1073	Ag	0.000	N	Y			
1077	Bg	0.000	N	Y			
1082	Ag	0.000	N	Y	1086	7	Ph-NO$_2$ stretch
1086	Bg	0.000	N	Y			
1087	Au	3.632	Y	N			
1088	Bu	4.798	Y	N			
1146	Au	0.032	Y	N	1149	5	$\mathcal{M}27$
1148	Bu	0.427	Y	N			
1151	Bg	0.000	N	Y			
1152	Ag	0.000	N	Y			
1160	Au	0.042	Y	N	1165	9	$\mathcal{M}7$
1164	Ag	0.000	N	Y			
1167	Bg	0.000	N	Y			
1169	Bu	0.376	Y	N			
1291	Bg	0.000	N	Y	1293	4	$\mathcal{M}26$
1293	Au	0.337	Y	N			
1294	Ag	0.000	N	Y			
1295	Bu	0.080	Y	N			
1310	Ag	0.000	N	Y	1317	14	N–O$_2$ sym stretch
1314	Au	33.571	Y	N			
1318	Bu	31.886	Y	N			
1324	Bg	0.000	N	Y			
1361	Au	0.898	Y	N	1362	3	$\mathcal{M}25$
1362	Bu	1.849	Y	N			
1362	Ag	0.000	N	Y			
1364	Bg	0.000	N	Y			
1444	Ag	0.000	N	Y	1445	2	$\mathcal{M}24$
1445	Bu	0.004	Y	N			
1445	Au	0.048	Y	N			
1446	Bg	0.000	N	Y			
1460	Bu	2.114	Y	N	1461	1	$\mathcal{M}5$
1460	Ag	0.000	N	Y			
1461	Au	1.989	Y	N			
1462	Bg	0.000	N	Y			
1502	Ag	0.000	N	Y	1506	16	N–O$_2$ asym stretch
1502	Au	10.741	Y	N			
1503	Bu	36.908	Y	N			
1518	Bg	0.000	N	Y			
1578	Au	0.687	Y	N	1579	3	$\mathcal{M}4$
1579	Bg	0.000	N	Y			
1579	Bu	1.490	Y	N			
1580	Ag	0.000	N	Y			

1594	Au	0.068	Y	N	1597	6	$\mathcal{M}23$
1598	Ag	0.000	N	Y			
1598	Bg	0.000	N	Y			
1600	Bu	1.746	Y	N			
3126	Bg	0.000	N	Y	3126	1	$\mathcal{M}3$
3126	Ag	0.000	N	Y			
3126	Bu	0.529	Y	N			
3127	Au	0.217	Y	N			
3133	Bu	0.109	Y	N	3133	1	$\mathcal{M}22$
3133	Au	0.108	Y	N			
3134	Ag	0.000	N	Y			
3134	Bg	0.000	N	Y			
3144	Au	0.051	Y	N	3144	1	$\mathcal{M}2$
3144	Bu	0.058	Y	N			
3145	Bg	0.000	N	Y			
3145	Ag	0.000	N	Y			
3157	Bu	1.123	Y	N	3158	1	$\mathcal{M}21$
3157	Ag	0.000	N	Y			
3158	Au	0.300	Y	N			
3158	Bg	0.000	N	Y			
3160	Bu	0.946	Y	N	3161	0	$\mathcal{M}1$
3160	Au	1.300	Y	N			
3161	Ag	0.000	N	Y			
3161	Bg	0.000	N	Y			

[a]Transition energy.

[b]Symmetry of the factor group component.

[c]Average value of the four factor group components.

[d]Difference between the highest and lowest energy of the four factor group components.

[e]Assignments using the Gardner and Wright $\mathcal{M}$i notation [38] (see Figure S2 and Table S1).

Table S3. Experimental and calculated geometry of nitrobenzene.[a]

	Experimental		Calculated				
	Gas[b]	Solid[b]	Isolated (Gaus)	Isolated (CASTEP)	Adsorbed (para)	Adsorbed (perp)	Solid
Symmetry	C_{2v}	C_1	C_{2v}	C_{2v}	C_s	C_s	C_1
Distance / Å							
C–C	C1C2 1.385 C2C3 1.401 C3C4 1.389	C1C2 1.387, C2C3 1.384, C3C4 1.387, C4C5 1.389, C5C6 1.383, C6C1 1.385	C1C2 1.388, C2C3 1.388, C3C4 1.392	C1C2 1.394 C2C3 1.395 C3C4 1.399	C1C2 1.459 C2C3 1.432 C3C4 1.452	C1C2 1.402, C2C3 1.392, C3C4 1.399, C4C5 1.400, C5C6 1.392, C6C1 1.402	C1C2 1.396, C2C3 1.392, C3C4 1.398, C4C5 1.397, C5C6 1.391, C6C1 1.395
C–N	1.468	1.465	1.477	1.491	1.508	1.431	1.474
N–O	1.223	NO1 1.223, NO2 1.229	1.221	1.224	1.228	NO1(Pd) 1.270 NO2 1.260	NO1 1.229, NO2 1.229
C–H	C2H 1.069 C3H 1.072 C4H 1.073	C1H 0.931, C2H 0.946 C3H 0.954, C4H 1.030, C5H 0.904	C2H 1.079, C3H 1.081, C4H 1.082	C2H 1.087 C3H 1.088 C4H 1.089	C2H 1.088 C3H 1.089 C4H 1.094	C1H 1.086, C2H 1.089 C3H 1.089, C4H 1.089, C5H 1.087	C1H 1.085, C2H 1.086 C3H 1.087, C4H 1.086, C5H 1.085
Angle / °	C1C2C3 117.8 C2C3C4 120.3, C3C4C5 120.5, C6C1C2 123.5 C2C1N 118.2 C1NO 117.9 ONO 124.2	C1C2C3 118.1, C2C3C4 120.2, C3C4C5 120.5, C4C5C6 120.3, C5C6C1 118.1, C6C1C2 122.8 C2C1N 118.8 C6C1N 118.4 C1NO1 118.2 C1NO2 118.6 ONO 123.2	C1C2C3 118.5, C2C3C4 120.3, C3C4C5 120.2, C2C1C2 122.3, C2C1N 118.8, C1NO 117.7, ONO 124.7	C1C2C3 118.5 C2C3C4 120.2, C3C4C5 120.3, C6C1C2 122.3 C2C1N 118.8 C1NO 117.5 ONO 125.1	C1C2C3 121.0 C2C3C4 121.9, C3C4C5 116.8, C6C1C2 122.3 C2C1N 116.0 C1NO 117.6 ONO 124.7	C1C2C3 118.6, C2C3C4 120.5, C3C4C5 120.0, C4C5C6 120.5, C5C6C1 118.6, C6C1C2 121.7 C2C1N 119.3 C6C1N 118.9 C1NO1 118.5 C1NO2 119.2 ONO 122.3	C1C2C3 118.4, C2C3C4 120.1, C3C4C5 120.5, C4C5C6 120.2, C5C6C1 118.3, C6C1C2 122.4 C2C1N 118.9 C6C1N 118.8 C1NO1 118.0 C1NO2 118.3 ONO 123.7

Planar?	Yes	No, NO_2 1.7° rotated	Yes	Yes	No, NO_2 and C–H bent away from plane of ring	Yes	No, NO_2 1.0° rotated

[a]Symmetry related values are not given

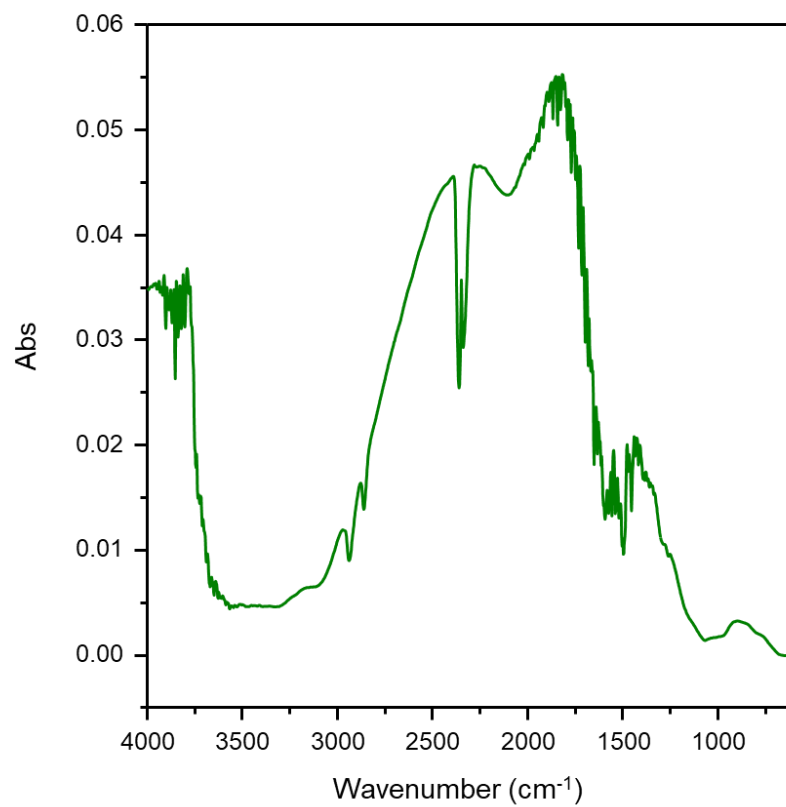[b]r_e structure (Table 9 of reference [38])

[c][32]

<u>Figure S3</u>.   Single beam DRIFTS measurement of activated GU-1.

Section S1: Nitrobenzene Tilting - $C_s\,\sigma_v(xz)$ Symmetry

Evidence of differing adsorbate geometry as a function of surface coverage would only be observable for nitrobenzene exhibiting $C_s\,\sigma_v(xz)$ symmetry, as observed for a parallel adsorption orientation, and a change of orientation in the molecular xz-plane. For a parallel orientation of nitrobenzene over a metal surface, the in-plane A' $v_S(NO_2)$ mode (Figure S4a).) would not be observed, as per the MSSR [12], [14], due to a parallel orientation of the resulting dipole to the metal surface. The perpendicular orientation of the out-of-plane A' $\delta_{oop}(CH)$ mode (Figure S4b).) would yield a perpendicularly positioned dipole, and thus would be IR allowed. If the orientation of nitrobenzene was changed in the xz-plane such that the molecule retained $C_s\,\sigma_v(xz)$ symmetry but was now positioned in a titled orientation (Figure S4(c-d).) both the in-plane $v_S(NO_2)$ and out-of-plane $\delta_{oop}(CH)$ modes would be observed. Therefore, spectra would change from presenting solely out-of-plane modes, to all IR allowed modes.

Figure S4.   Visualisation of the $v_S(NO_2)$ and $\delta_{oop}(CH)$ nitrobenzene modes during (a-b) a parallel orientation and (c-d) a tilted adsorption orientation over a metal surface with respect to the molecules xz-plane. Orange arrows indicate the dipole derivative unit vector associated with each mode. Grey parallelograms symbolise a non-specific Pd crystallite.
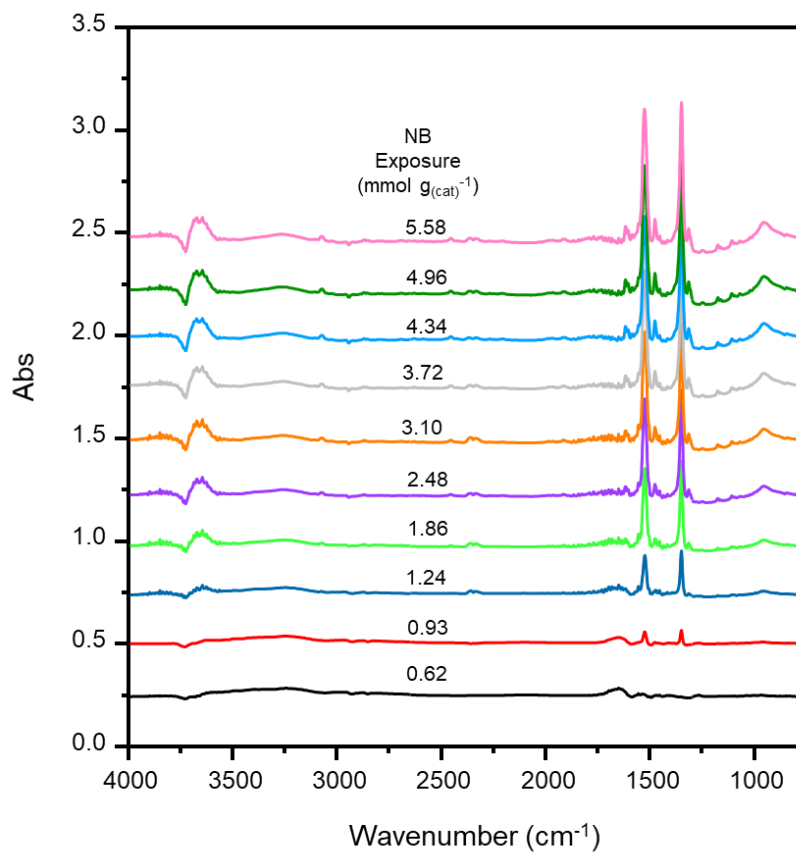
Figure S5.   Full wavenumber range DRIFTS spectra depicting increasing nitrobenzene exposure (0.62 – 5.58 $mmol_{(NB)}$ $g_{(cat)}^{-1}$) to GU-1. The spectra have been offset by 0.25 au to facilitate viewing.

1: 124.7°
2: 117.7°
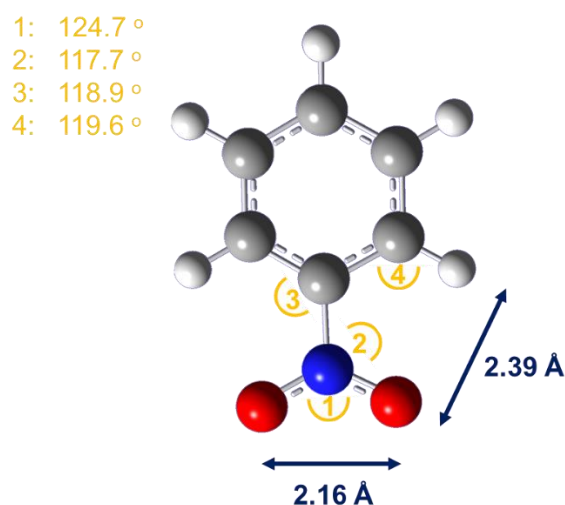3: 118.9°
4: 119.6°

2.39 Å

2.16 Å

Figure S6.   Nitrobenzene molecule depicting theoretical intra-atomic distances and bond angles derived using the B3LYP method and 6-11G++(3df.2p) basis set.

This investigation is unable to state an exact tilt angle associated with nitrobenzene adsorption to the catalyst and was not principally focused on ascertaining such. However, consideration of geometrical parameters associated with nitrobenzene and bulk Pd can be used to estimate the positioning of molecular adsorption over Pd(111), the pre-dominant metal surface associated with GU-1 [24], [25]. Literature reports an interatomic Pd-Pd distance of 2.75 Å [49]; from geometrical considerations, this corresponds to distances from the on-top Pd site to the 3-fold hollow site and the adjacent 2-fold hollow to be 1.20 and 2.39 Å, respectively.

The DFT optimised nitrobenzene structure reports distances of 2.16 Å for the two O atoms of the nitro group and 2.39 Å as the distance between one O atom and the closest ortho-H of the aromatic ring, as depicted in Figure S6. The 2.16 Å between the two O atoms of the nitro group does not correspond with the interatomic Pd-Pd (2.75 Å), the on-top Pd to 3-fold hollow site (1.20 Å) or the on-top Pd to 2-fold hollow site (2.39 Å) distances. However, the intra-atomic distance between one O of the nitro group and the closest ortho-H atom (2.39 Å) is coincident with the distance between the on-top and the adjacent 2-fold hollow site. Therefore, we suggest that nitrobenzene adsorbs to the Pd crystallite in a tilted orientation with respect to the molecules yz-plane via two close contacts: (i). the ortho-H atom is in registry with the on-top site, and the O atom is positioned above the adjacent 2-fold hollow site (Fig. S7(a)), or (ii) the O atom is in registry with the on-top site, and the ortho-H is positioned above the adjacent 2-fold hollow site (Fig. S7(b)). Either of these orientational arrangements would act to maximise substrate-adsorbate and adsorbate-adsorbate (via π-stacking) interactions. The specifics of which sites discreetly interact with each atom are not known and would benefit from a full DFT

investigation of the adsorption complex; something that is beyond the scope of the current article. Nevertheless, instinctively, it is assumed that option (i), with the O atom located in the 2-fold hollow of the (111) plane, which is depicted in Figure S7, will exhibit the stronger overall interaction with the surface (*i.e.,* high $T_{desorption}$) as indicated in TP-IR (Fig. 10).
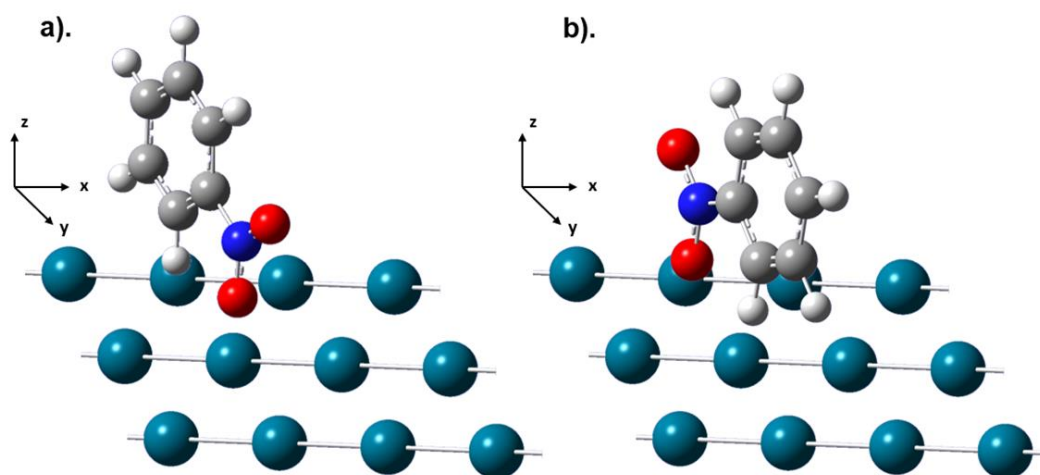

Figure S7.   Diagram visualising nitrobenzene adsorption to Pd(111) in a tilted orientation with respect to the yz-plane depicting a). O positioned in a 2-fold hollow site with H in registry with on-top and b). the H positioned in a 2-fold hollow site with O in registry with the on-top site.