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

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As part of an on-going programme of development of an aniline synthesis catalyst suitable for operation at elevated temperatures, the geometry of the adsorption complex for nitrobenzene on a 5 wt% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst is investigated by infrared (IR) spectroscopy. *Via* an appreciation of the reduced site symmetry resulting from adsorption, application of the metal surface selection rule, and observation of in-plane modes only, the adsorption complex (Pd–nitrobenzene) at 28 °C is assigned as occurring vertically or tilted with respect to the metal surface, adopting C<sub>s</sub>σ<sub>v</sub>(yz) symmetry. Moreover, adsorption occurs *via* a single Pd–O bond. Single molecule DFT calculations and simulated IR spectra assist vibrational assignments but indicate a parallel adsorption geometry to be energetically favourable. The contradiction between calculated and observed structures is attributed to the DFT calculations corresponding to an isolated molecule adsorption complex, while IR spectra relate to multi molecule adsorption that is encountered during sustained catalytic turnover. Residual hydrogen from the catalyst reduction stage leads to aniline formation on the Pd surface at low nitrobenzene coverages but, on increasing nitrobenzene exposure, the aniline is forced on to the alumina support. A reaction scheme is proposed whereby the nitrobenzene adsorption geometry is inherently linked to the high aniline selectivity observed for Pd/Al<sub>2</sub>O<sub>3</sub> catalysts.

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## 1. Introduction

The heterogeneously catalysed hydrogenation of nitrobenzene is a commonly employed route to produce aniline, which in

turn is a key component in the formation of methylene diphenyl diisocyanate (MDI) utilised throughout the polyurethane industry.<sup>1</sup> Supported Pd catalysts are regularly described as achieving high aniline selectivity from nitrobenzene hydrogenation<sup>2–9</sup> owing to the high activity and propensity of Pd to reduce functional groups in proximity to aromatic structures. The current investigation aims to investigate nitrobenzene adsorption over a reference Pd/Al<sub>2</sub>O<sub>3</sub> catalyst *via* infrared (IR) spectroscopy to better understand the origins of this favourable aniline selectivity.

Nitrobenzene and aniline both possess a phenyl ring and a functional group moiety, permitting the possibility of various interactions between the molecules and a catalyst surface. It follows that each of these potential interactions may result in different preferential orientations of nitrobenzene and aniline on metal surfaces – a parameter which may be directly related to catalytic outputs. A DFT study by Chen *et al.* highlighted the possible relationship between observed chemical pathways and adsorbate geometry, where 100% product selectivity during hydrogenation of *p*-chloronitrobenzene using platinum nanoparticles encapsulated into zeolite Y as a catalyst was reported.<sup>10</sup> This perfect selectivity was attributed to an end-on orientation of *p*-chloronitrobenzene enforced by steric constraints of the zeolite pore size.

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† Electronic supplementary information (ESI) available: Fig. 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; Fig. S2: Form of the vibrational modes for a mono-substituted benzene in C<sub>2v</sub> symmetry; Table S1: Approximate wavenumber ranges for the *ν*<sub>i</sub> vibrations; Table S2: Vibrational transition energies, infrared intensities and assignments for nitrobenzene in the solid state as calculated by periodic-DFT; Fig. S3: Single beam DRIFTS measurement of activated GU-1; Table S3: Experimental and calculated geometry of nitrobenzene; Fig. S4: Wide scan DRIFTS spectra depicting increasing nitrobenzene exposure; Fig. S5: Visualisation of the *ν*<sub>5</sub>(NO<sub>2</sub>) and *δ*<sub>oop</sub>(CH) nitrobenzene modes during a (a) and (b) parallel orientation and (c) and (d) a tilted adsorption orientation over a metal surface with respect to the molecules xz-plane; Fig. S6: 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. See DOI: <https://doi.org/10.1039/d3cp03028h>



The geometry of adsorbates may be inferred from IR spectra with reference to the metal surface selection rule (MSSR):<sup>11</sup> molecular vibrations that yield a dipole parallel to a metal surface are unobservable, whilst vibrations yielding a non-parallel dipole to a metal surface are observable.<sup>12,13</sup>

The IR spectrum of nitrobenzene ( $C_{2v}$  symmetry) has been extensively described,<sup>14–17</sup> with two high intensity peaks centred around 1530 and 1350  $\text{cm}^{-1}$  assigned to the in-plane asymmetric ( $B_2$  symmetry) and symmetric ( $A_1$  symmetry)  $\text{NO}_2$  stretching modes of nitrobenzene ( $\nu_{\text{AS}}(\text{NO}_2)$  and  $\nu_{\text{S}}(\text{NO}_2)$ ), respectively, being the most prominent features. In addition, several out-of-plane  $B_1$  symmetry modes are observed, including a moderate intensity band at *ca.* 705  $\text{cm}^{-1}$  that corresponds to the out-of-plane  $\text{NO}_2$  deformation mode ( $\delta_{\text{oop}}(\text{NO}_2)$ ) and smaller features centred at *ca.* 935 and 793  $\text{cm}^{-1}$ , both arising from out-of-plane C–H deformation modes ( $\delta_{\text{oop}}(\text{CH})$ ).<sup>14,15</sup>

Surface science studies are insightful. Richardson and co-workers used reflection–absorption infrared spectroscopy (RAIRS) to investigate the adsorption of nitrobenzene on Cu(110) over a range of temperatures.<sup>18</sup> For temperatures < 223 K multilayer adsorption was observed, with no preferential orientation of the nitrobenzene molecule relative to the metal surface. Adsorption at 300 K led to dissociation of the nitrobenzene. A subsequent vibrational electron energy loss spectroscopy study established the retained moieties to be phenyl species and atomic oxygen.<sup>18</sup> Koel and co-workers used RAIRS to investigate the adsorption of nitrobenzene on Au(111) at low temperatures.<sup>19</sup> For monolayer coverages, only two bands were observed: an out-of-plane CH deformation at 793  $\text{cm}^{-1}$  and a  $\text{NO}_2$  deformation at 710  $\text{cm}^{-1}$ . Assuming  $C_{2v}$  symmetry, these modes exhibit  $B_1$  symmetry, indicating the nitrobenzene molecule to be aligned parallel to the surface. On increasing coverage, modes with  $A_1$  and  $B_2$  symmetry were observed, indicative of a change of molecular orientation. As neither in-plane nor out-of-plane modes are screened completely, the molecule was assumed to adopt a tilted geometry. Temperature-programmed desorption measurements showed the monolayer to exhibit a desorption maximum at 290 K.<sup>19</sup> Bridging the gap between surface science and heterogeneous catalysis, Corma and co-workers have examined the adsorption of nitroaromatics on Au single crystal surfaces and supported Au particles.<sup>20</sup> For the case of nitrostyrene adsorption, the Au/support interface was reported to be the active site of Au/TiO<sub>2</sub>, which exhibits high chemo-selectivity *via* preferential activation of the nitro group.

Density functional theory (DFT) is widely used to investigate adsorbate orientation, and has been utilised to investigate the adsorption geometry of nitrobenzene on varying systems. A recent study by Hajiahmadi *et al.* considered the likelihood of six different nitrobenzene adsorption configurations, three vertical and three parallel, over Pd(111).<sup>21</sup> They found a parallel nitrobenzene adsorption geometry with N atoms located on top of Pd atoms to be most favourable for adsorption to Pd(111). Additionally, Boronat *et al.* conducted a DFT investigation into nitroarene adsorption primarily over non-noble metals, with the inclusion of Pd(111) for comparison, and report parallel

nitrobenzene adsorption over Pd(111) *via* the aromatic ring with the  $\text{NO}_2$  group twisted relative to the aromatic moiety.<sup>22</sup> Interestingly, Boronat and co-workers reported strictly perpendicular nitrobenzene adsorption over the non-noble metal Cu(111) and used this specified adsorbate geometry to propose a possible non-noble metal catalyst candidate for high selectivity aniline synthesis. Contrarily for Pd studies, a DFT investigation of nitrobenzene adsorption on bimetallic Pd<sub>3</sub>/Pt(111) found vertical nitrobenzene adsorption over Pd crystallites to be preferable to parallel adsorption.<sup>23</sup> Comparison of these opposing outcomes indicates that nitrobenzene adsorption orientation is substrate dependent. This perspective meshes with a recent spectroscopic and computational study by Millán and co-workers on nitrobenzene activation on non-noble metals-based mono- and bimetallic catalysts.<sup>24</sup>

This article concentrates on the adsorption of nitrobenzene over a 5 wt% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst (GU-1) that is a model for low metal loading Pd/Al<sub>2</sub>O<sub>3</sub> aniline synthesis catalysts intended for operation at elevated temperatures.<sup>8</sup> The performance of this catalyst in vapour phase nitrobenzene hydrogenation has previously been described,<sup>8</sup> as has the morphology of the Pd crystallites.<sup>25</sup> The approach adopted is as follows. A complete vibrational analysis of nitrobenzene is undertaken with reference to measured solid and liquid phase spectra (inelastic neutron scattering, infrared spectroscopy, and Raman scattering). The infrared spectrum of nitrobenzene adsorbed on GU-1 is compared to simulated spectra corresponding to DFT calculations for the adsorption of a single unit of nitrobenzene on a Pd(111) surface, providing information on the geometry of the adsorption complex. The unidentate nature of the interaction between the nitro group and the Pd surface is consistent with established reaction schemes. A small quantity of aniline is formed at the Pd surface at low nitrobenzene exposures, but it is forced on to the alumina support on increasing nitrobenzene exposure. A reaction scheme is proposed whereby the nitrobenzene adsorption geometry is inherently linked to the high aniline selectivity observed for Pd/Al<sub>2</sub>O<sub>3</sub> catalysts.

## 2. Experimental

A 5 wt% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was obtained from Alfa Aesar (ref.: 11713). The catalyst has been comprehensively characterised<sup>25</sup> and is referred to here, and in previous communications from this group,<sup>8,25</sup> as GU-1.

### 2.1 Computational methods

The Gaussian09<sup>26</sup> and GaussView software packages were used to derive the vibrational spectrum of gas phase nitrobenzene. Density functional theory (DFT) was utilised with the B3LYP functional and the 6-311G++(3df,2p) basis set. A DFT scaling factor of 0.967 was used on calculated wavenumbers.<sup>27</sup> Solid state calculations used the plane wave pseudopotential method as implemented in CASTEP.<sup>28</sup> The generalized gradient approximation (GGA) was used with the PBE functional.<sup>29</sup> The Tkatchenko and Scheffler-dispersion correction was used to



account for the long-range interactions.<sup>30</sup> For nitrobenzene, the initial structure used the experimental crystal structure that was determined at 103 K.<sup>31</sup> The plane wave cut-off was 1020 eV and the Brillouin zone sampling used a  $12 \times 4 \times 4$  (48 *k*-points) Monkhorst–Pack grid. The adsorption of nitrobenzene on Pd(111) was investigated using a three-layer slab with (111) truncation. A 15 Å vacuum gap was used. For both the parallel and vertical orientations, the plane wave cut-off was 1020 eV and the Brillouin zone sampling used a  $11 \times 11 \times 1$  (36 *k*-points) Monkhorst–Pack grid. After geometry optimisation, the vibrational transition energies were calculated with density functional perturbation theory.<sup>32</sup> To reduce the time required for the calculation, only the internal modes of the nitrobenzene were calculated. The computational outputs include the amplitude of motion of each atom in the vibrational mode, this enables mode visualisation and enables the inelastic neutron scattering (INS) spectrum to be calculated using the program AbINS.<sup>33</sup>

In Section 3.2.3 Gaussian calculations are used to simulate the IR spectra for nitrobenzene adopting parallel and vertical adsorption geometries relative to the Pd surface. Here, with consideration of point group theory and the MSSR, simulated spectra for parallel ( $C_s\sigma_v(xz)$ ) and mono-dentate vertical ( $C_s\sigma_v(yz)$ ) nitrobenzene adsorption over a metal surface were produced by adjusting the intensity of non-accessible modes to 0 a.u.

## 2.2 Vibrational spectroscopy

Infrared spectra (256 scans,  $4 \text{ cm}^{-1}$  resolution, eight-times zero-filling) of nitrobenzene were measured with a Bruker Vertex 70 Fourier transform infrared (FT-IR) spectrometer. The liquid at room temperature was measured by attenuated total internal reflection (ATR) using a Bruker Diamond ATR accessory. Variable temperature (210–296 K) spectra were recorded with a low temperature SpecAc Golden Gate ATR accessory. Raman spectra were recorded with a Bruker Fourier transform Raman spectrometer (64 scans,  $4 \text{ cm}^{-1}$  resolution, eight-times zero-filling, 500 mW laser power at 1064 nm). The sample was held in a quartz cuvette and the liquid measured at room temperature and the solid after immersion of the cuvette in liquid nitrogen. INS spectra of the solid were recorded at 10 K from the sample held in a flat-plate indium wire sealed aluminium can using the broad band, high resolution spectrometer TOSCA<sup>34</sup> at ISIS.<sup>35</sup>

## 2.3 DRIFTS measurements: nitrobenzene adsorption and temperature-programmed IR spectroscopy

*In situ* DRIFTS measurements were performed with a Bruker Vertex 70 FT-IR spectrometer fitted with a MCT detector. GU-1 was supplied as a powder and was used directly. *Ca.* 50 mg of GU-1 was placed into a Harrick Praying Mantis DRIFTS reaction chamber. A Harrick ATC heater permitted control of cell temperature. Activation of Pd crystallites occurred *in situ* using a flow of helium ( $35 \text{ mL min}^{-1}$ , BOC gases, 99.9%) and hydrogen ( $15 \text{ mL min}^{-1}$ , BOC gases, 99.8%) while heating to  $110 \text{ }^\circ\text{C}$ . This temperature was held for 30 minutes. The temperature was then increased to  $200 \text{ }^\circ\text{C}$  for one hour, with the

hydrogen flow stopped after 30 minutes and the sample allowed to return to ambient temperature in flowing He. A He purge of 18 hours was utilised to minimise the levels of retained hydrogen within GU-1 from the reduction process, which would otherwise result in nitrobenzene hydrogenation to aniline. Post-purge, a background spectrum was collected at  $28 \text{ }^\circ\text{C}$ .

Nitrobenzene was supplied *via* a nitrobenzene bubbler system which supplied  $61.2 \mu\text{mol}_{(\text{NB})} \text{min}^{-1} g_{(\text{cat})}^{-1}$  to the reaction chamber in the vapour phase using He as a carrier gas. A 5-minute pulse duration was selected, so that 1 pulse corresponded to a nitrobenzene exposure of  $0.31 \text{ mmol}_{(\text{NB})} g_{(\text{cat})}^{-1}$ . After each pulse, the cell was purged with He for 10 minutes to evacuate unbound nitrobenzene before spectral acquisition.

For desorption experiments, the catalyst was heated *in situ* under a flow of He and maintained at the designated temperature for 30 minutes before cooling to  $28 \text{ }^\circ\text{C}$  for spectral acquisition. This process was repeated for 50, 100, 120, 140, 160, 180 and  $200 \text{ }^\circ\text{C}$ . All spectra were recorded at  $28 \text{ }^\circ\text{C}$  for 520 scans at  $4 \text{ cm}^{-1}$  resolution. Spectra are presented as difference spectra, where the spectrum of the activated catalyst has been subtracted from that of a nitrobenzene dosed spectrum. No additional spectrum treatment was performed. A minor aniline impurity was present in the feed stream to the IR cell, which could not be eliminated. Though vexatious, its minimal presence in the IR spectra can be accounted for and will be suitably considered in the following sections.

## 3. Results

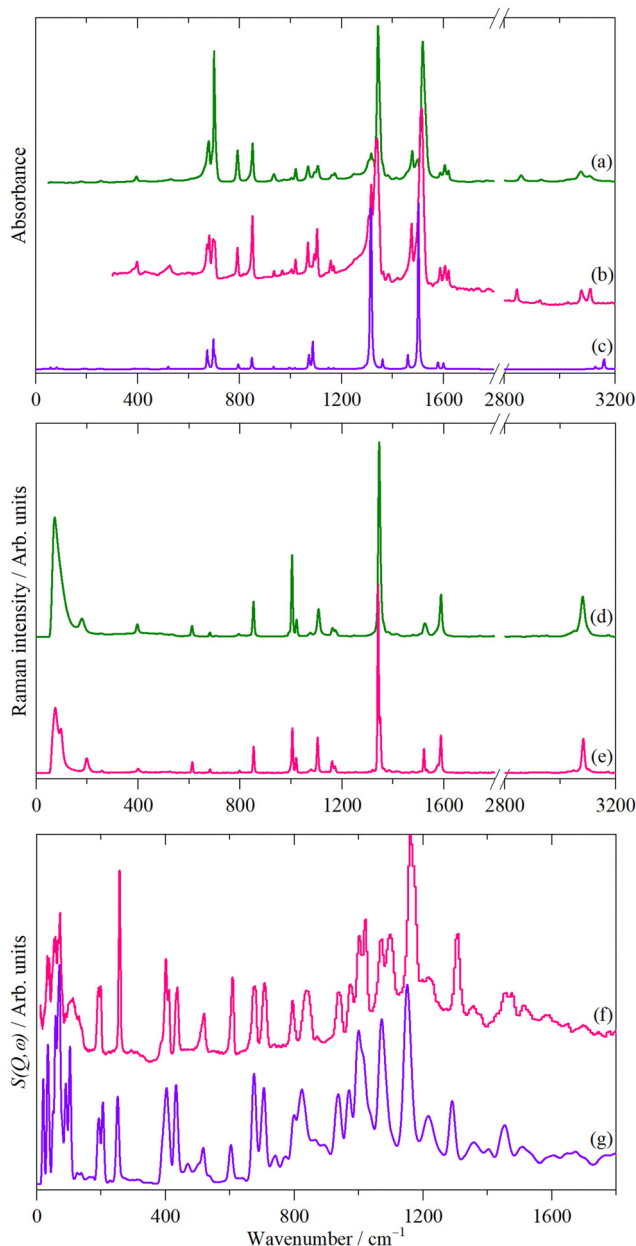
### 3.1 Molecular symmetry and DFT: assigning key nitrobenzene modes

In the gas and liquid phases nitrobenzene exhibits  $C_{2v}$  symmetry,<sup>36</sup> see Fig. S1 in the ESI† In the solid state, there are four molecules in the primitive cell, each on a site with  $C_1$  symmetry, however, the  $C_{2v}$  symmetry is largely retained.<sup>31</sup> Reference to the  $C_{2v}$  character table confirms modes possessing  $A_1$ ,  $B_1$  and  $B_2$  symmetry are infrared active.<sup>37</sup>

Fig. 1 shows the infrared and Raman spectra in the liquid phase, the infrared, Raman, and INS spectra in the solid state, together with the calculated infrared and INS spectra for the solid state. Table 1 presents experimental wavenumber values and DFT-derived frequencies for nitrobenzene in the liquid phase. The vibrational spectra of mono-substituted benzenes have been extensively studied over the decades and the various schemes are lucidly discussed by Gardner and Wright.<sup>38</sup> Based on DFT calculations, they proposed some revision to the assignments and designated the modes as  $\mathcal{M}1$ – $\mathcal{M}30$ . The form of the modes and their usual ranges are reproduced from ref. 38 in the ESI† (Fig. S2 and Table S1). We have adopted their assignment scheme and the vibrational assignments and associated symmetry designations are also listed in Table 1.

In the solid state, the presence of four molecules in the primitive cell results in factor group splitting. However, periodic-DFT calculations of the complete unit cell show that





**Fig. 1** Experimental and calculated vibrational spectra of nitrobenzene. Top panel: infrared spectra of (a) liquid nitrobenzene at room temperature, (b) solid nitrobenzene at 210 K, (c) calculated spectrum for solid nitrobenzene. Middle panel: Raman spectra of (d) liquid nitrobenzene at room temperature, (e) solid nitrobenzene. Bottom panel: INS spectrum (f) solid nitrobenzene at 10 K and (g) calculated spectrum for solid nitrobenzene.

for most of the internal modes this is  $10 \text{ cm}^{-1}$  or less, although there are exceptions (see Table S2, ESI<sup>†</sup>). These are the Ph-NO<sub>2</sub> torsion and some of the out-of-plane C-H bending modes. As can be seen from Fig. 1, the calculated infrared and INS spectra are in good agreement with the experimental data (*cf.* Fig. 1b, c and f, g).

As mentioned in the Introduction, owing to their high intensity,<sup>14,21</sup> the  $B_2$  symmetry  $\nu_{\text{AS}}(\text{NO}_2)$  and  $A_1$  symmetry  $\nu_{\text{S}}(\text{NO}_2)$  modes at  $1531$  and  $1348 \text{ cm}^{-1}$  respectively, represent key nitrobenzene modes for orientational diagnostics. The IR spectrum of activated GU-1 is presented in Fig. S3 (ESI<sup>†</sup>) and

**Table 1** Comparison of experimental and DFT-derived wavenumbers ( $\text{cm}^{-1}$ ) of nitrobenzene. DFT calculations performed utilising the B3LYP method and 6-311G++(3df,2p) basis set. Vibrational assignments are based on DFT calculations

Mode	Sym.	Expt. <sup>a</sup>	DFT <sup>b</sup>	Assignment		
1	A <sub>2</sub>	52 <sup>c</sup>	57	$\tau(\text{Ph-NO}_2)$		oop
2	B <sub>1</sub>	179	164	$\delta_{\text{oop}}(\text{Ph-NO}_2)$	M20	oop
3	B <sub>2</sub>	256	249	$\delta_{\text{ip}}(\text{Ph-NO}_2)$	M30	ip
4	A <sub>1</sub>	396	383	Ring deformation	M11	ip
5	A <sub>2</sub>	423	404	Ring deformation	M14	oop
6	B <sub>1</sub>	454 <sup>c</sup>	432	Ring deformation	M19	oop
7	B <sub>2</sub>	529	508	NO <sub>2</sub> rock		ip
8	B <sub>2</sub>	608	607	$\delta_{\text{ip}}(\text{CCC})$	M29	ip
9	B <sub>1</sub>	677	663	$\delta_{\text{oop}}(\text{CH})$	M18	oop
10	A <sub>1</sub>	680	671	$\delta_{\text{ip}}(\text{ring}) + \delta_{\text{ip}}(\text{NO}_2) + \nu(\text{CN})$	M10	ip
11	B <sub>1</sub>	700	704	NO <sub>2</sub> wag + $\delta_{\text{oop}}(\text{CH})$	M17 <sup>d</sup>	oop
12 <sup>e</sup>	B <sub>1</sub>	793	791	NO <sub>2</sub> wag + $\delta_{\text{oop}}(\text{CH})$	M17 <sup>d</sup>	oop
13	A <sub>2</sub>	837	831	$\delta_{\text{oop}}(\text{CH})$	M13	oop
14	A <sub>1</sub>	851	839	NO <sub>2</sub> scissors		ip
15 <sup>e</sup>	B <sub>1</sub>	935	936	$\delta_{\text{oop}}(\text{CH})$	M16	oop
16	A <sub>2</sub>	975	972	$\delta_{\text{oop}}(\text{CH})$	M12	oop
17	A <sub>1</sub>	977	977	$\delta_{\text{ip}}(\text{ring})$	M9	ip
18	B <sub>1</sub>	991	988	$\delta_{\text{oop}}(\text{CH})$	M15	oop
19	A <sub>1</sub>	1003	1006	$\delta_{\text{ip}}(\text{ring})$	M8	ip
20	B <sub>2</sub>	1069	1063	$\delta_{\text{ip}}(\text{CH})$	M28	ip
21	A <sub>1</sub>	1094	1078	$\nu(\text{Ph-NO}_2)$	M6	ip
22	B <sub>2</sub>		1145	$\delta_{\text{ip}}(\text{CH})$	M27	ip
23	A <sub>1</sub>	1162	1157	$\delta_{\text{ip}}(\text{CH})$	M7	ip
24	B <sub>2</sub>	1248	1294	$\delta_{\text{ip}}(\text{CH})$	M26	ip
25	B <sub>2</sub>	1308	1305	$\nu(\text{CC})$	M25	ip
26 <sup>e</sup>	A <sub>1</sub>	1344	1348	$\nu_{\text{S}}(\text{NO}_2)$		ip
27	B <sub>2</sub>	1415	1439	$\nu(\text{CC})$	M24	ip
28	A <sub>1</sub>	1478	1462	$\nu(\text{CC})$	M5	ip
29 <sup>e</sup>	B <sub>2</sub>	1528	1531	$\nu_{\text{AS}}(\text{NO}_2)$		ip
30	A <sub>1</sub>	1588	1572	$\nu(\text{CC})$	M4	ip
31	B <sub>2</sub>	1606	1596	$\nu(\text{CC})$	M23	ip
32	A <sub>1</sub>	3029	3066	$\nu(\text{CH})$	M3	ip
33	B <sub>2</sub>	3077	3079	$\nu(\text{CH})$	M22	ip
34	A <sub>1</sub>		3086	$\nu(\text{CH})$	M2	ip
35	B <sub>2</sub>	3107	3116	$\nu(\text{CH})$	M21	ip
36	A <sub>1</sub>	3107	3117	$\nu(\text{CH})$	M1	ip

<sup>a</sup> Experimental wavenumbers for nitrobenzene are from Fig. 1a, or otherwise indicated. <sup>b</sup> Scaling factor for DFT frequencies was 0.967.<sup>40</sup> <sup>c</sup> Ref. 41. <sup>d</sup> This mode appears twice because it is mixed with the NO<sub>2</sub> wag. <sup>e</sup> Key diagnostic modes for orientational assignments in the present investigation.

exhibits a spectral cut-off due to strong Al-O phonon modes of the alumina support<sup>39</sup> at about  $1100 \text{ cm}^{-1}$ . With respect to Table 1, in the presence of the catalyst, several  $B_1$  symmetry diagnostic nitrobenzene modes are inaccessible; for example, the  $\delta_{\text{oop}}(\text{NO}_2)$  feature present at  $704 \text{ cm}^{-1}$ . However, rather fortuitously, GU-1's  $\gamma$ -alumina displays a narrow transmission window in the  $970\text{--}745 \text{ cm}^{-1}$  range (Fig. S3, ESI<sup>†</sup>), which enables access to two  $\delta_{\text{oop}}(\text{CH})$   $B_1$  symmetry modes at  $791$  and  $936 \text{ cm}^{-1}$ , respectively. Therefore, on this basis, vibrational transitions 12, 15, 26 and 29 (Table 1) were selected as key modes for orientational diagnostics.

### 3.2 DRIFTS: adsorbate geometry

**3.2.1 Nitrobenzene adsorption on KBr at 28 °C.** Fig. 2b presents the spectrum of nitrobenzene adsorbed on KBr



at 28 °C. The spectrum is indicative of physisorbed nitrobenzene with no specific orientation, and yields all four key nitrobenzene modes (Table 1): the  $B_2$  symmetry  $\nu_{AS}(\text{NO}_2)$  mode at 1529  $\text{cm}^{-1}$ , the  $A_1$  symmetry  $\nu_S(\text{NO}_2)$  mode at 1347  $\text{cm}^{-1}$  and the two  $B_1$  symmetry  $\delta_{oop}(\text{CH})$  modes at 935 and 793  $\text{cm}^{-1}$ .<sup>14,15</sup> This measurement confirmed the capability of the DRIFTS set-up utilised to observe all  $A_1$ ,  $B_1$  and  $B_2$  symmetry key diagnostic modes.

### 3.2.2 Saturation nitrobenzene coverage on GU-1 at 28 °C.

Fig. 2a presents the IR spectrum for a saturation coverage of nitrobenzene over GU-1 at 28 °C. As observed for KBr (Fig. 2b), the  $A_1$  and  $B_2$  symmetry modes at 1529 and 1347  $\text{cm}^{-1}$  are present but, intriguingly, the  $B_1$  symmetry modes at 935 and 793  $\text{cm}^{-1}$  were not observed.

The observation of  $A_1$  and  $B_2$  key modes and absence of  $B_1$  modes in spectra associated with nitrobenzene adsorption to the catalyst provides information on the form of the adsorption complex. However, prior to assignment of molecular geometry utilising the MSSR, it is essential to consider the impact of binding to a metal surface on the molecular symmetry of nitrobenzene; thus, reference to the  $C_{2v}$  correlation table is necessary.  $C_{2v}$  symmetry correlates to four lower symmetry point groups:<sup>37</sup>  $C_1$ ,  $C_2$ ,  $C_s\sigma_v(xz)$  and  $C_s\sigma_v(yz)$ , where  $C_s\sigma_v(xz)$  and  $C_s\sigma_v(yz)$  represent a molecule possessing  $C_s$  symmetry with a single mirror plane in the molecule's  $xz$  and  $yz$ -planes, respectively.

Table 2 considers the accessibility of each key nitrobenzene diagnostic mode during nitrobenzene adsorption to a metal surface in a vertical or parallel orientation for nitrobenzene exhibiting  $C_{2v}$ ,  $C_2$ ,  $C_s\sigma_v(xz)$  and  $C_s\sigma_v(yz)$  symmetry. With reference to this table, at a saturation coverage of nitrobenzene, Fig. 2a indicates that nitrobenzene exhibits  $C_s\sigma_v(yz)$  symmetry

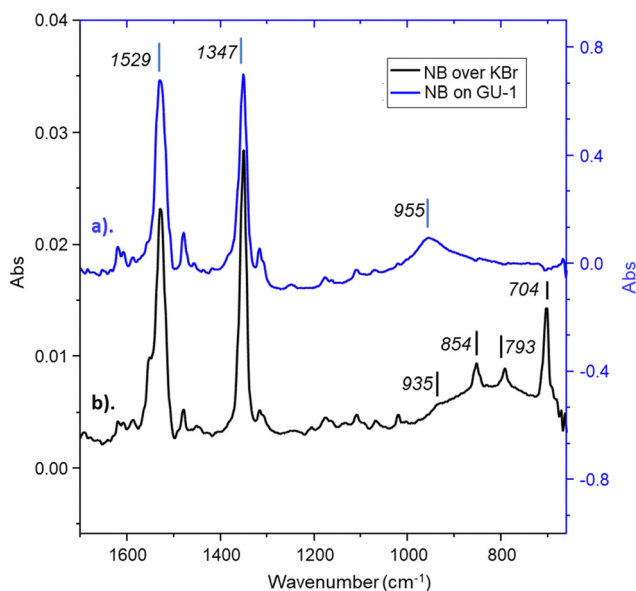


Fig. 2 DRIFTS spectra of nitrobenzene adsorption over (a) GU-1 (blue) and (b) KBr (black) at 28 °C. Wavenumber range: 1700–660  $\text{cm}^{-1}$ . Note the differences in y-axes scales for both spectra.

Table 2 Assignment, wavenumber values and symmetric representations for key nitrobenzene diagnostic modes

Assign.	Expt. <sup>a</sup> ( $\text{cm}^{-1}$ )	Symmetric Representations											
		$C_{2v}$		$C_2$		$C_s\sigma_v(xz)$		$C_s\sigma_v(yz)$					
		$\perp^b$	$\parallel^c$	$\perp^b$	$\parallel^c$	$\perp^b$	$\parallel^c$	$\perp^b$	$\parallel^c$				
$\text{NO}_2$ wag + $\delta_{oop}(\text{CH})$	794	$B_1$	N	Y	$B_2$	N	Y	$A'$	Y	Y	$A''$	N	<sup>d</sup>
$\delta_{oop}(\text{CH})$	935	$B_1$	N	Y	$B_2$	N	Y	$A'$	Y	Y	$A''$	N	<sup>d</sup>
$\nu_S(\text{NO}_2)$	1351	$A_1$	Y	N	$A_2$	Y	N	$A'$	Y	N	$A''$	Y	<sup>d</sup>
$\nu_{AS}(\text{NO}_2)$	1527	$B_2$	N	N	$B_1$	N	N	$A''$	Y	N	$A'$	Y	<sup>d</sup>

<sup>a</sup> Experimental wavenumbers for nitrobenzene are from Fig. 1a.

<sup>b</sup> Indicates if mode is allowed during vertical nitrobenzene adsorption over a metal surface, as per the MSSR.<sup>11</sup> N = no; Y = yes. <sup>c</sup> Indicates if mode is allowed during parallel nitrobenzene adsorption over a metal surface, as per the MSSR.<sup>11</sup> N = no; Y = yes. <sup>d</sup> Corresponding orientation is not possible for nitrobenzene exhibiting stated symmetric representation.

and is positioned in a vertical orientation over the metal surface; a deduction that contradicts previously introduced DFT investigations.<sup>20,21</sup>

For nitrobenzene to exhibit  $C_s\sigma_v(yz)$  symmetry adsorption must occur *via* only one Pd–O bond (Fig. 3(c and d)); as binding to the Pd surface *via* both oxygens of the nitro group would retain the  $C_{2v}$  symmetry of nitrobenzene (Fig. 3(a and b)). For vertical nitrobenzene bidentate adsorption ( $C_{2v}$  symmetry) the  $\nu_S(\text{NO}_2)$  and  $\nu_{AS}(\text{NO}_2)$  modes exhibit  $A_1$  and  $B_2$  symmetry, respectively. For the  $A_1$   $\nu_S(\text{NO}_2)$  (Fig. 3b) the resulting dipole

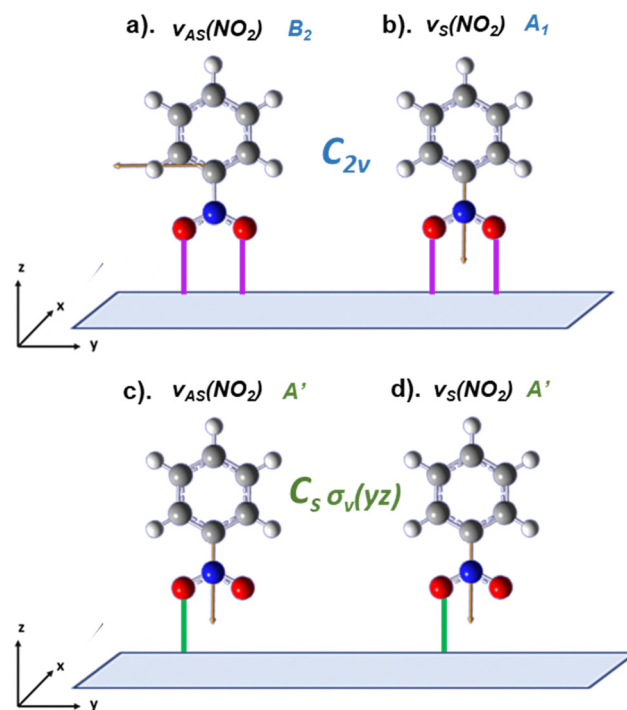


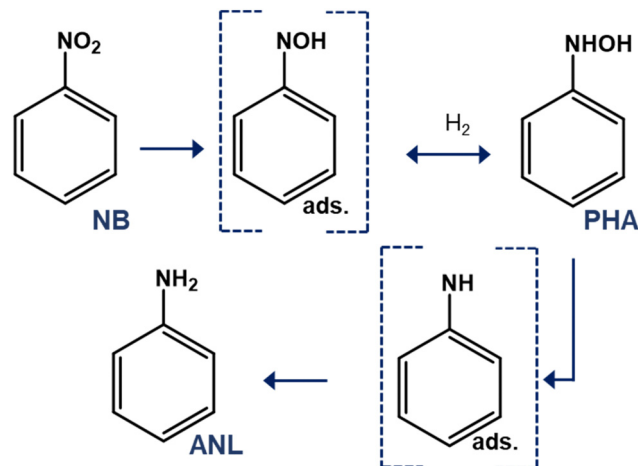
Fig. 3 Visualisation of  $\nu_S(\text{NO}_2)$  and  $\nu_{AS}(\text{NO}_2)$  nitrobenzene modes during vertical adsorption over a metal surface *via* (a) and (b) bidentate and (c) and (d) monodentate binding. Orange arrows indicate the dipole derivative unit vector associated with each mode. Grey parallelograms symbolise a non-specific Pd crystallite. White, grey, blue and red balls represent hydrogen, carbon, nitrogen and oxygen, respectively.



(Fig. 3, orange arrow) is positioned perpendicularly to the metal surface, thus with consideration of the MSSR, this mode would be observed in IR spectra,<sup>11,13</sup> as is the case during adsorption to GU-1. However, the dipole associated with the  $B_2$  symmetry  $\nu_{AS}(\text{NO}_2)$  mode (Fig. 3a) is aligned parallel to the metal surface during bidentate vertical adsorption, and resultingly, would not be observable in IR spectra. Thus, a bidentate vertical adsorption of nitrobenzene to the metal surface, and thus retention of  $C_{2v}$  symmetry during binding, is not possible as both the  $A_1$   $\nu_S(\text{NO}_2)$  and  $B_2$   $\nu_{AS}(\text{NO}_2)$  symmetry modes of nitrobenzene were clearly observed during adsorption to GU-1 (Fig. 2a). Conversely, for monodentate vertical nitrobenzene adsorption ( $C_s\sigma_v(yz)$ ) both the  $\nu_S(\text{NO}_2)$  and  $\nu_{AS}(\text{NO}_2)$  modes correlate to  $A'$  symmetry, and so are both totally symmetric in-plane modes (Fig. 3(c and d)). The resulting dipole for each  $A'$  mode during a vertical nitrobenzene adsorption would be positioned perpendicular to the metal surface and would therefore be MSSR allowed. Thus, nitrobenzene adsorbs to the Pd crystallites of GU-1 in a vertical orientation *via* monodentate binding, and not bidentate binding of the metal group. Moving forward, nitrobenzene modes will be referred to as exhibiting either  $A'$  or  $A''$  symmetry as encountered for  $C_s\sigma_v(yz)$  symmetry (Table 2).

The known chemistry of metal catalysed nitrobenzene hydrogenation is supportive of the proposed geometric structure. A scenario in which both O atoms of nitrobenzene simultaneously interacted with the metal would result in a rapid and simultaneous one-step hydrogenation of the nitro group with no observable intermediates. However, as reported by Gelder *et al.*, hydrogenation of the nitro moiety occurs in a stepwise fashion, and intermediates such as phenylhydroxylamine (PHA) are accessible during nitrobenzene hydrogenation with Pd (Scheme 1).<sup>42</sup> Moreover, this observable intermediate, PHA, exhibits  $C_s\sigma_v(yz)$  symmetry, further strengthening the hypothesis of nitrobenzene exhibiting the same symmetry during adsorption to GU-1. Thus, we assert that the assignment of  $C_s\sigma_v(yz)$  symmetry and monodentate binding for nitrobenzene adsorption over the catalyst is consistent with the reported chemistry.

The authors acknowledge the totally vertical orientation depicted in Fig. 3(c and d) may be an over-simplification, as it is not possible to entirely differentiate if nitrobenzene exhibiting  $C_s\sigma_v(yz)$  symmetry adsorbs vertically, or if the molecule exhibits some degree of tilting in the  $yz$ -plane. Fig. 4(a and b) presents visualisation of the in-plane  $A'$  symmetry  $\nu_S(\text{NO}_2)$  and out-of-plane  $A''$  symmetry  $\delta_{\text{opp}}(\text{CH})$  modes of nitrobenzene whilst exhibiting  $C_s\sigma_v(yz)$  symmetry in a tilted orientation, and highlights the respective perpendicular and parallel alignment of resulting dipoles with respect to the metal surface. The non-parallel orientation of the  $A'$  symmetry dipole will permit observation of the  $\nu_S(\text{NO}_2)$  mode in IR spectra (Fig. 4a), while the parallel orientation of the out-of-plane  $A''$  dipole will yield the  $\delta_{\text{opp}}(\text{CH})$  mode unobservable (Fig. 4b).<sup>11,13</sup> Thus, nitrobenzene adsorption orientation may be visualised as occurring vertically, or with some degree of tilting in the molecules  $yz$ -plane. For completeness, Fig. S4 (ESI†) presents a visualisation of nitrobenzene aligned with respect to the molecule's  $xz$ -plane and eliminates the option of either vertical or tilted variants in that plane.



Scheme 1 A schematic representation for aniline (ANL) formation via the stepwise hydrogenation of nitrobenzene (NB) to phenylhydroxylamine (PHA) over a supported Pd catalyst as reported by Gelder and co-workers. Blue hashed boxes represent surface species. The figure has been adapted from Chemical Communications.<sup>42</sup>

Small frequency shifts were observed when comparing wavenumber values for the key  $\nu_{AS}(\text{NO}_2)$  and  $\nu_S(\text{NO}_2)$  modes during nitrobenzene adsorption over KBr (Fig. 2b) to adsorption over GU-1 (Fig. 2a) from 1529 to 1530  $\text{cm}^{-1}$  and 1347 to 1352  $\text{cm}^{-1}$ , respectively. A larger wavenumber shift upon adsorption was anticipated; not least because Section 3.2.5 reveals an appreciable enthalpy of adsorption over GU-1. One possible scenario is that dipole coupling effects<sup>43</sup> are contributing to the spectrum of the bound nitrobenzene *via* two opposing effects: a dipole coupling shift which acts to increase wavenumber values for high coverages, and a chemical shift that results in a lowering of wavenumber values.<sup>43</sup> RAIRS spectra reported by Koel and co-workers depicting increasing nitrobenzene coverage over Au(111) obtained *via* RAIRS do not exhibit any discernible frequency shift either.<sup>19</sup>

An additional broad feature centred at 955  $\text{cm}^{-1}$  is clearly discernible for the IR spectrum depicting nitrobenzene adsorption to GU-1 (Fig. 2a); this peak cannot be assigned to any nitrobenzene vibrational mode (Table 1). The origins of this band will be addressed further in Section 3.2.4.

**3.2.3 Computational studies.** In the previous section it was proposed that nitrobenzene is chemisorbed on the Pd nanoparticles in a vertical/tilted configuration *via* one Pd–O bond. In this section we investigate by periodic-DFT the extreme possibilities, *i.e.* where the plane of the phenyl ring is oriented perpendicular or parallel to the metal surface. As a model system, we have used a three-layer slab of Pd, cleaved along (111) with a 15 Å vacuum gap. For both orientations, there is a mirror plane perpendicular to the surface. The results are shown in Fig. 5. Parallel adsorption results in a significant distortion of the molecule with the nitro group and the hydrogens bent away from the plane of the molecule (see Table S3, ESI†), with the molecule exhibiting  $C_s\sigma_v(xz)$  symmetry. This is reminiscent of the ligand distortions found in metal cyclopentadienyl (*e.g.* ferrocene<sup>44</sup>) and metal arene complexes (*e.g.* bisbenzene chromium<sup>45</sup>).



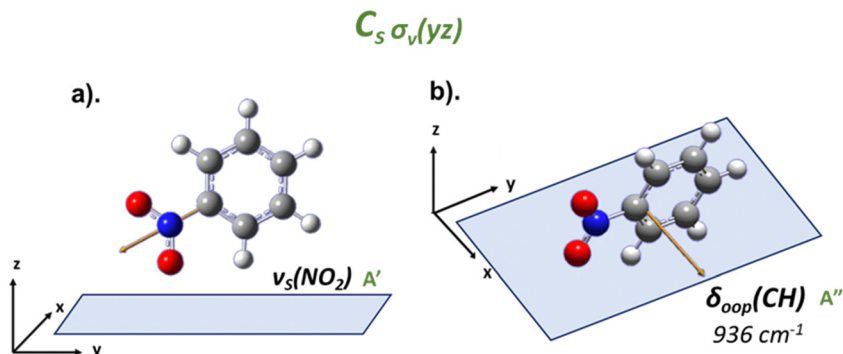


Fig. 4 Visualisation of (a).  $\nu_s(\text{NO}_2)$  and (b).  $\delta_{\text{oop}}(\text{CH})$  nitrobenzene modes during a tilted adsorption orientation over a metal surface with respect to the molecules  $yz$ -plane. Orange arrows indicate the dipole derivative unit vector associated with each mode. Grey parallelograms symbolise a non-specific Pd crystallite. White, grey, blue and red balls represent hydrogen, carbon, nitrogen and oxygen, respectively.

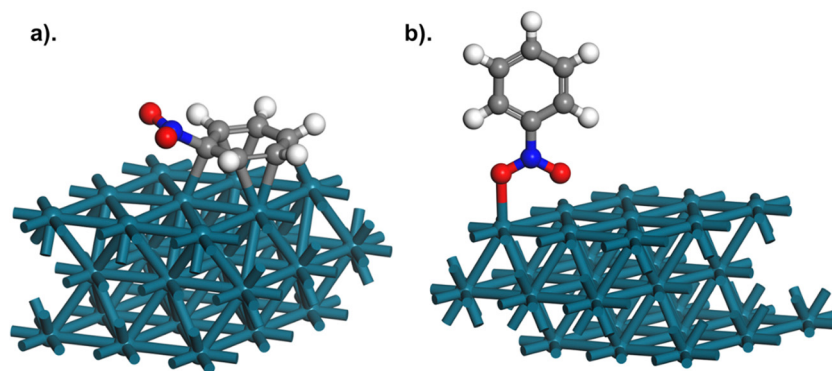


Fig. 5 Geometry optimised periodic-DFT structures of nitrobenzene adsorbed parallel (a) and perpendicular (b) on the Pd(111) facet. White, grey, blue and red balls represent hydrogen, carbon, nitrogen and oxygen, respectively.

The optimised structure for nitrobenzene adsorbed on Pd(111) was recently reported by Millán and co-workers<sup>24</sup> as occurring in a parallel orientation *via* binding of the phenyl group and *via* a single N-O...Pd, with the C-H bonds distorted from the plane of the molecule and the NO<sub>2</sub> group twisted with respect to the phenyl ring. In contrast, our calculations show perpendicular adsorption results in only minimal changes in the molecular geometry. Consistent with the infrared studies (Section 3.2.2), monodentate adsorption *via* a N-O...Pd interaction is found.

The adsorption energy ( $E_{\text{ads}}$ , kJ mol<sup>-1</sup>) can be calculated from:

$$E_{\text{ads}} = [\text{Pd}(111) + \text{nitrobenzene}] - [\text{Pd}(111)] - [\text{nitrobenzene}], \quad (1)$$

where the terms in square brackets refer to the energies of the adsorbate complex (*i.e.*, as shown in Fig. 3), the clean surface and the free molecule, respectively. This gives  $E_{\text{ads}} = -366$  and  $-99.3$  kJ mol<sup>-1</sup> for the parallel and perpendicular adsorption geometries, respectively.

That the parallel geometry is the lowest energy state is a surprising result. Fig. 6 presents the experimental spectrum of nitrobenzene adsorption over GU-1 and the simulated spectra for parallel ( $C_s\sigma_v(xz)$ ) and monodentate vertical ( $C_s\sigma_v(yz)$ ) nitrobenzene adsorption over a metal surface. The simulated spectra

are obtained *via* the process described in Section 2.1. For a parallel adsorption, the simulated spectrum (Fig. 6a) depicts the absence of the in-plane  $\nu_{\text{AS}}(\text{NO}_2)$  and  $\nu_s(\text{NO}_2)$  modes usually visualised at *ca.* 1350 and 1530 cm<sup>-1</sup> as per the MSSR. However, these modes are clearly observed during adsorption to GU-1 (Fig. 2a). In distinct contrast, the simulated spectrum for a monodentate nitrobenzene adsorption complex does present these modes and, crucially, it does not include any out-of-plane  $A''$  symmetry modes, as observed experimentally (Fig. 2a). Thus, comparison between the simulated  $C_s\sigma_v(yz)$  symmetry vertical nitrobenzene adsorption spectrum (Fig. 6b) and experimental outcomes herewith is distinct, and clearly identifies nitrobenzene adsorption over GU-1 to result in an adsorption complex in which nitrobenzene exhibits  $C_s\sigma_v(yz)$  symmetry, and not the proposed  $C_s\sigma_v(xz)$  symmetry from simulated outcomes. Additionally, the pronounced distortion that nitrobenzene undergoes on parallel adsorption is not intuitive to a favourable geometry.

Relative to the ideal  $C_{2v}$  geometry of gas phase nitrobenzene, the parallel form of nitrobenzene is 113.1 kJ mol<sup>-1</sup> higher in energy, while the perpendicular form is only 7.9 kJ mol<sup>-1</sup> higher. The stabilisation of the parallel form presumably reflects that there are six Pd-C bonds, whereas there is a single Pd-O bond for the perpendicular form. Thus, we have



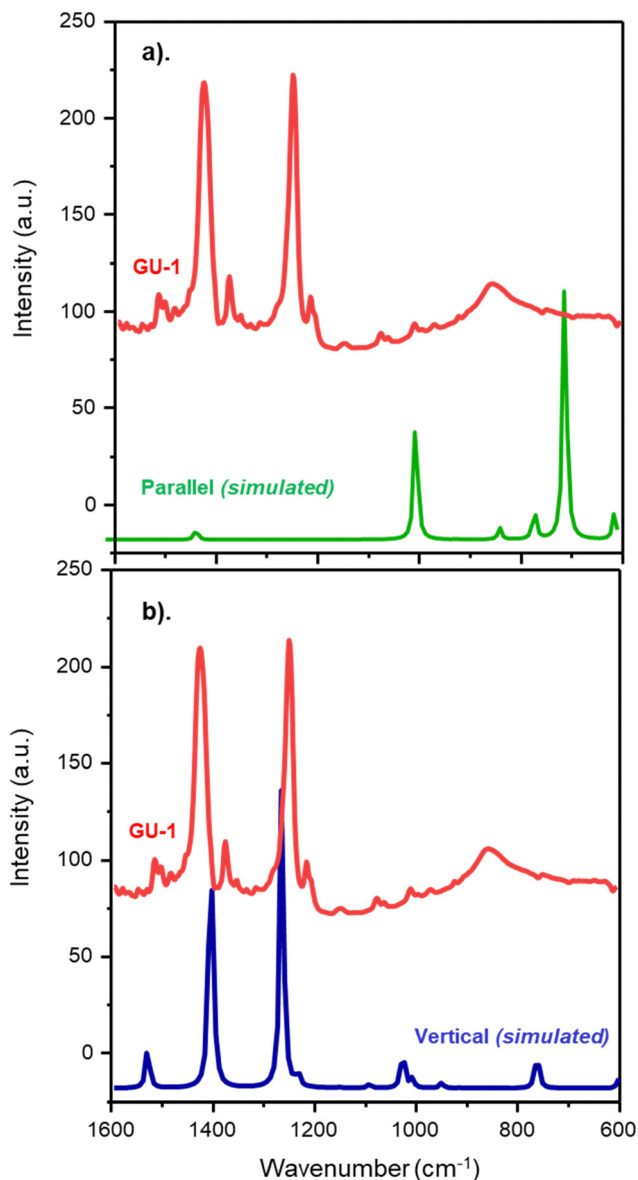


Fig. 6 DRIFTS spectrum of nitrobenzene adsorption to GU-1 (red) alongside the simulated spectrum for (a) parallel and (b) monodentate vertical nitrobenzene adsorption over a metal surface. Wavenumber range: 1600–600  $\text{cm}^{-1}$ .

an interesting result and an apparent conundrum: the measured IR spectrum strongly correlates with nitrobenzene adopting a vertical/tilted geometry relative to the metal surface with binding occurring *via* a single O atom (Fig. 5b), whilst the energetics emanating from the calculations strongly indicate a preference for a distorted parallel geometry (Fig. 5a).

The authors note that the calculations correspond to a single adsorption event that does not account for any ensemble effects from intermolecular interactions between multiple molecular adsorptions; a scenario that is not wholly indicative of elevated nitrobenzene exposures as encountered in catalytic turnover. Specifically, GU-1 possesses a Pd surface density of  $1.153 \times 10^{20} \text{ Pd}_{(\text{s})} \text{ g}^{-1.25}$  and the incident nitrobenzene flux is

$3.68 \times 10^{19} \text{ NB molecules min}^{-1} \text{ g}^{-1}$  (Section 2.3) that corresponds to a continuous incident flux of 0.32 NB molecules  $\text{min}^{-1} \text{ Pd}_{(\text{s})}^{-1}$ . The lowest nitrobenzene exposure examined ( $0.62 \text{ mmol}_{(\text{NB})} \text{ g}_{(\text{cat})}^{-1}$ ) corresponds to a cumulative exposure of  $1.87 \times 10^{22}$  nitrobenzene molecules, which translates to 3234 nitrobenzene molecules  $\text{Pd}_{(\text{s})}^{-1}$ . Thus, even the lowest nitrobenzene exposures considered here correspond to a multi-monolayer coverage regime as encountered during catalytic turnover, which is differentiated from the single molecule coverage regime examined by the DFT calculations. Under these conditions, adsorbate–adsorbate interactions will prevail. Additionally, the Pd crystallites of GU-1, which represents a real working catalytic system,<sup>8</sup> may present a level of complexity not accessible *via* modelling on a perfect Pd(111) surface.

These reasonings represent suggestions for the encountered conundrum and highlight difficulties to be considered when applying a combination of *in situ* structural determination and isolated molecule DFT simulated structures within the field of heterogeneous catalysis. Summarising, nitrobenzene adsorption corresponding to aniline synthesis is thought to require the nitrobenzene to adopt an upright/tilted geometry with  $C_s\sigma_v(yz)$  symmetry, as illustrated in Fig. 5b.

**3.2.4 Surface coverage investigation: nitrobenzene adsorption at 28 °C.** Fig. 7 presents spectra for nitrobenzene adsorption to GU-1 for the wavenumber range 1700–700  $\text{cm}^{-1}$ . The full range for all spectra can be found in the supporting information (Fig. S5, ESI†). Characteristic nitrobenzene spectral features arising from the  $A'$  symmetry  $\nu_{\text{AS}}(\text{NO}_2)$  and  $\nu_{\text{S}}(\text{NO}_2)$  modes were observed post-exposure to  $0.93 \text{ mmol}_{(\text{NB})} \text{ g}_{(\text{cat})}^{-1}$ , centred at 1529 and 1347  $\text{cm}^{-1}$ , respectively. IR bands arising

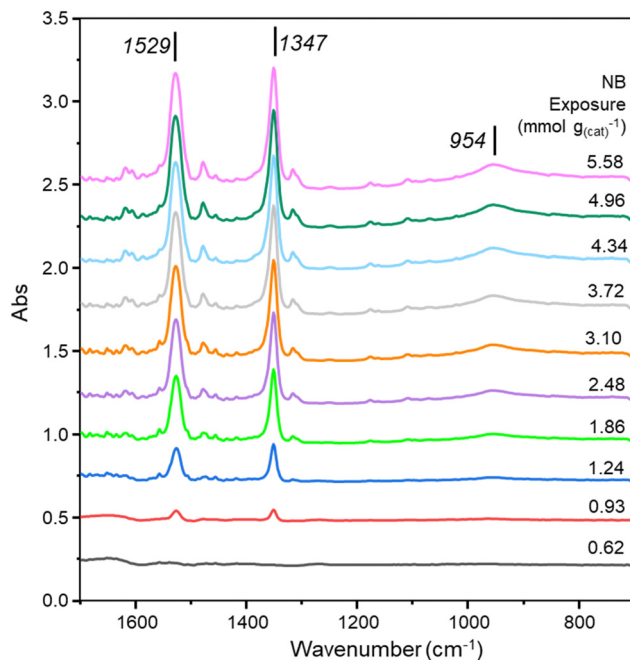


Fig. 7 DRIFTS spectra depicting increasing nitrobenzene exposure ( $0.62$ – $5.58 \text{ mmol}_{(\text{NB})} \text{ g}_{(\text{cat})}^{-1}$ ) to the catalyst at 28 °C. The spectra have been offset by 0.25 au to facilitate viewing. Wavenumber range: 1700–700  $\text{cm}^{-1}$ .



from  $A'$  symmetry modes associated with the aromatic moiety of nitrobenzene were first observable after introduction of  $1.24 \text{ mmol}_{(\text{NB})} \text{ g}_{(\text{cat})}^{-1}$ . For example, ring stretching ( $\nu(\text{CC})$ ) modes at 1607, 1585, 1476, 1415 and  $1317 \text{ cm}^{-1}$ ; and a series of in-plane C–H bending modes ( $\delta_{\text{ip}}(\text{CH})$ ) at *ca.*  $1300\text{--}1000 \text{ cm}^{-1}$ . No IR features corresponding to out-of-plane  $A''$  symmetry nitrobenzene modes were observable for nitrobenzene exposures  $\leq 5.58 \text{ mmol}_{(\text{NB})} \text{ g}_{(\text{cat})}^{-1}$ .

As briefly considered in Section 3.2.2, a broad feature centred at  $954 \text{ cm}^{-1}$  is observed at saturation coverages (Fig. 2a) that is not assigned to any nitrobenzene vibrational mode. Fig. 8 presents spectra for nitrobenzene exposures of 0.62 and  $0.93 \text{ mmol}_{(\text{NB})} \text{ g}_{(\text{cat})}^{-1}$  only and reveals a series of bands at 1647, 1271 and  $954 \text{ cm}^{-1}$  after the initial  $0.62 \text{ mmol}_{(\text{NB})} \text{ g}_{(\text{cat})}^{-1}$  exposure. Aniline possesses a  $\text{NH}_2$  bending mode ( $\delta_{\text{oop}}(\text{NH}_2)$ ), a C–N stretching mode ( $\nu(\text{CN})$ ) and a series of C–H deformation modes ( $\delta(\text{CH})$ ) at *ca.* 1628, 1278 and  $996\text{--}883 \text{ cm}^{-1}$ ,<sup>46,47</sup> respectively. Thus, with reference to Fig. 8, we attribute the observation of stated wavenumber values at  $0.62 \text{ mmol}_{(\text{NB})} \text{ g}_{(\text{cat})}^{-1}$  exposure to the formation of aniline on the catalyst, with the  $\delta_{\text{oop}}(\text{NH}_2)$  mode exhibiting a notable shift in wavenumber, and assign the broad  $954 \text{ cm}^{-1}$  feature observed at a saturation coverage of nitrobenzene (Fig. 2a and 7) to a  $\delta(\text{CH})$  mode of aniline.<sup>46,47</sup> The intense and broad nature of this mode at nitrobenzene saturation coverage is anomalous and requires further investigation.

With reference to Fig. 7 and 8, the aniline features, excluding that of the broad band at *ca.*  $955 \text{ cm}^{-1}$ , are only observable at low nitrobenzene exposures. As they do not scale with nitrobenzene exposure ( $\leq 0.62 \text{ mmol}_{(\text{NB})} \text{ g}_{(\text{cat})}^{-1}$ ); *i.e.*, no nitrobenzene modes are observed, the aniline is thought to occur *via*

nitrobenzene hydrogenation *via* reaction with a small reservoir of residual hydrogen left over from the catalyst reduction stage. Thus, we have two sources of aniline adsorption to GU-1: (i) hydrogenation of nitrobenzene *via* a limited reservoir of sub-surface and surface hydrogen from reduction, as evidenced in Fig. 8, and (ii). *via* a minor aniline impurity within the experimental set-up.

Fig. 9 presents the intensity profile for the main IR bands observed in Fig. 7. At an exposure of  $0.62 \text{ mmol}_{(\text{NB})} \text{ g}_{(\text{cat})}^{-1}$  no  $\nu_{\text{AS}}(\text{NO}_2)$  and  $\nu_{\text{S}}(\text{NO}_2)$  features are observable but, thereafter, at higher exposures ( $\geq 0.93 \text{ mmol}_{(\text{NB})} \text{ g}_{(\text{cat})}^{-1}$ ) nitrobenzene coverage increases and approaches a plateau for nitrobenzene loadings exceeding  $4.96 \text{ mmol}_{(\text{NB})} \text{ g}_{(\text{cat})}^{-1}$ . The aniline intensity, as signified by the broad feature at  $954 \text{ cm}^{-1}$ , is seen to progressively increase as a function of nitrobenzene exposure. The separate profiles for nitrobenzene and aniline in Fig. 9 suggest separate adsorption sites on GU-1 for reagent and product. Summarising, for exposures of  $\geq 0.93 \text{ mmol}_{(\text{NB})} \text{ g}_{(\text{cat})}^{-1}$ , nitrobenzene adsorption on the Pd surface is seen to occur in a vertical/titled orientation in the  $yz$ -plane *via* one Pd–O bond independent of coverage, with the concomitant formation of aniline, which adsorbs in a different manner on GU-1.

**3.2.5 Temperature-programmed nitrobenzene desorption from GU-1.** Fig. 10 presents the temperature-programmed IR (TP-IR) spectra for a saturation dose of nitrobenzene over GU-1. No change in nitrobenzene adsorption geometry was observed with increasing desorption temperature; in-plane  $A'$  symmetry  $\nu_{\text{AS}}(\text{NO}_2)$  and  $\nu_{\text{S}}(\text{NO}_2)$  modes remained observable with no emergence of any out-of-plane  $A''$  symmetry ( $\delta_{\text{oop}}(\text{CH})$ ) derived nitrobenzene IR features. Thus, the form of the nitrobenzene adsorption complex is unchanged throughout the desorption

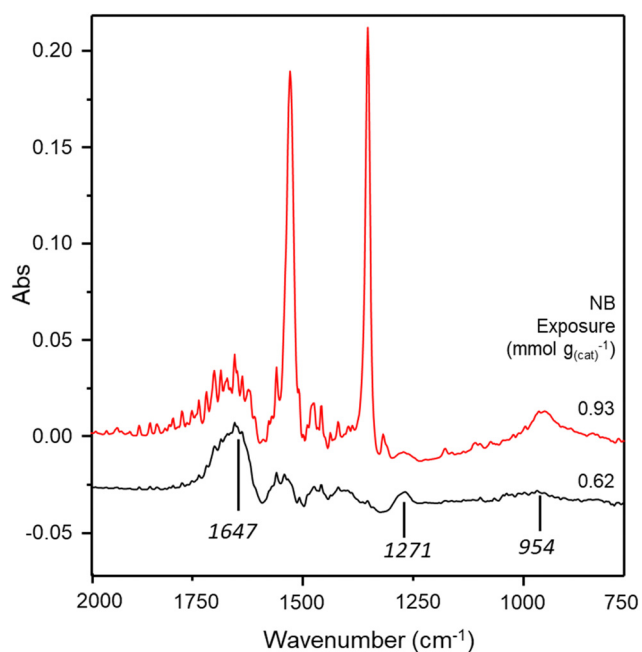


Fig. 8 DRIFTS spectra depicting nitrobenzene exposures of 0.62 (black) and  $0.93 \text{ mmol}_{(\text{NB})} \text{ g}_{(\text{cat})}^{-1}$  to the catalyst at  $28 \text{ }^\circ\text{C}$ . The spectra have been offset to facilitate viewing.

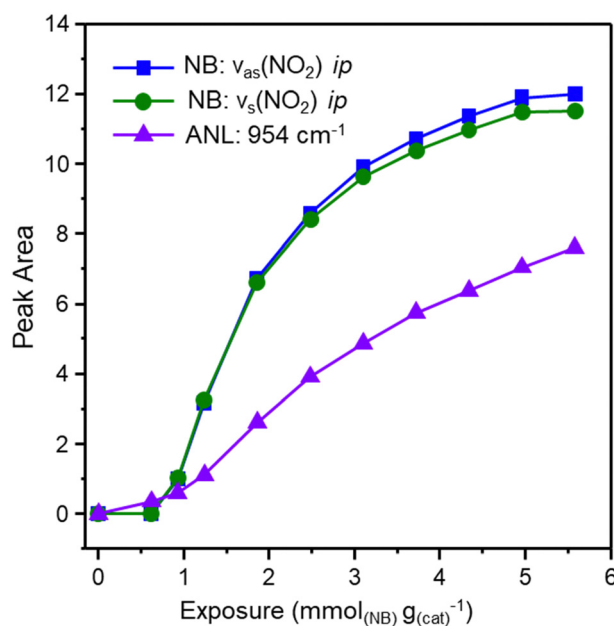


Fig. 9 Plot of peak area for nitrobenzene  $\nu_{\text{AS}}(\text{NO}_2)$  and  $\nu_{\text{S}}(\text{NO}_2)$  modes and aniline  $\delta(\text{CH})$  mode ( $954 \text{ cm}^{-1}$ ) as a function of increasing nitrobenzene exposure to GU-1 at  $28 \text{ }^\circ\text{C}$ .



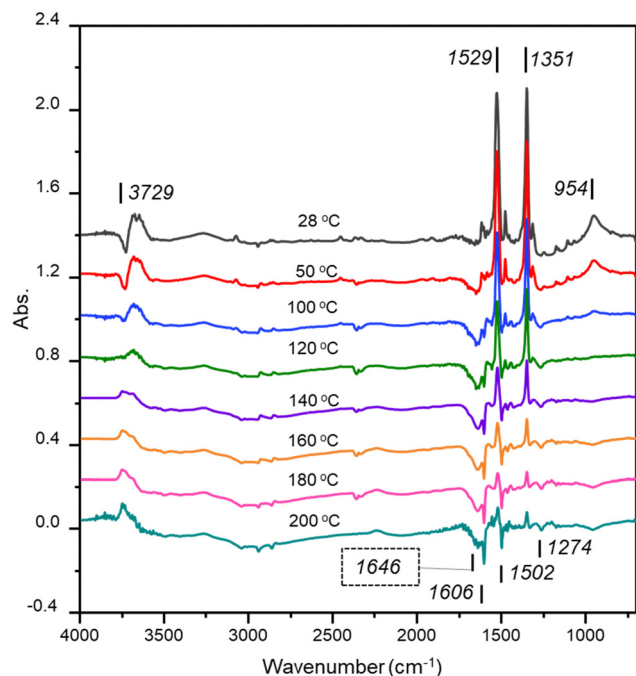


Fig. 10 DRIFTS spectra depicting nitrobenzene desorption from GU-1 with increasing temperature (28–200 °C). The spectra have been offset by 0.2 au to facilitate viewing.

phase depicted in Fig. 10 and remains in a vertical/tilted orientation with  $C_{2v}(yz)$  symmetry. A change of orientation in the  $xz$ -plane (Fig. S4, ESI†) would be distinct in IR spectra, as described in the ESI†

Although orientation of the reagent did not change with increasing desorption, several spectral changes are evident in Fig. 10. Firstly, the saturation coverage spectrum (Fig. 10, 28 °C) exhibits a negative peak at 3729  $\text{cm}^{-1}$  and a positive peak at 3677  $\text{cm}^{-1}$ . Surface hydroxyl groups of  $\gamma\text{-Al}_2\text{O}_3$  include terminal hydroxyls (type I) at *ca.* 3764  $\text{cm}^{-1}$ , bridging hydroxyls (type II) at *ca.* 3730  $\text{cm}^{-1}$ , and tri-bridged hydroxyls (type III) at *ca.* 3675  $\text{cm}^{-1}$ .<sup>48,49</sup> We therefore assign the negative IR feature at 3729  $\text{cm}^{-1}$  to bridging hydroxyl groups and the positive feature at 3677  $\text{cm}^{-1}$  to tri-bridging hydroxyl groups on the alumina support of GU-1, respectively.

All spectra presented have been background subtracted using a spectrum of the activated catalyst. Thus, the observed hydroxyl features suggest perturbation of the bridging and tri-bridged hydroxyl groups of the catalyst support. We propose the negative feature at 3729  $\text{cm}^{-1}$  observed at saturation coverage is indicative of a moiety forming a hydrogen bond to the bridging hydroxyl groups of the alumina support; this shifts the discrete  $\nu(\text{OH})$  to lower wavenumber, where it is submerged in the broad envelope of hydrogen-bonded hydroxyls. On background subtraction, this loss of the isolated  $\nu(\text{OH})$  leads to a negative feature. Similar observations have been reported over various aluminas during reagent adsorption.<sup>49–51</sup> As the desorption temperature is increased, the negative peak at 3729  $\text{cm}^{-1}$  decreases such that at 120 °C the negative hydroxyl feature is no longer observable, indicating desorption of the adsorbed

species from the bridging hydroxyl groups of the alumina support of GU-1 at this temperature. Crucially, at this temperature, the key in-plane  $A'$  symmetry modes ( $\nu_s(\text{NO}_2)$  and  $\nu_{\text{AS}}(\text{NO}_2)$ ) of nitrobenzene remain discernible, confirming that nitrobenzene adsorption occurred on the Pd crystallites of GU-1 and not the alumina support.

TP-IR measurements also revealed the emergence of derivative type features below 1700  $\text{cm}^{-1}$  with increasing desorption temperatures  $\geq 100$  °C. Four discernible negative intensity features were observed at 1646, 1606, 1502 and 1274  $\text{cm}^{-1}$ , and are assigned to aniline: the broad feature at 1646  $\text{cm}^{-1}$  corresponds to a shifted out-of-plane  $\text{NH}_2$  bending ( $\delta_{\text{oop}}(\text{NH}_2)$ ) mode, sharp bands at 1606 and 1502  $\text{cm}^{-1}$  correspond to in-plane ring stretching ( $\nu(\text{CC})$ ) modes and the feature at 1274  $\text{cm}^{-1}$  corresponds to the in-plane C–N stretching ( $\nu(\text{CN})$ ) mode.<sup>47</sup> These negative aniline bands are derived from the small aniline impurity within the experimental set-up, which permitted a limited degree of aniline adsorption to GU-1 prior to background collection (see Fig. 8). This small population of aniline is believed to be a ‘spectator’ species that does not affect observables concerning the nitrobenzene adsorption process. Thus, as referred to in Section 3.2.4, IR spectroscopy revealed the presence of two categories of adsorbed aniline that require accounting for. In the first instance, a small amount of aniline held as an impurity in the gas lines is present in the IR background spectrum. Secondly, low nitrobenzene exposures to GU-1 react with a small degree of retained hydrogen to form aniline that is adsorbed on metal sites (Fig. 8), with aniline shifted to the alumina support with increasing nitrobenzene exposure and represented by a broad feature at 954  $\text{cm}^{-1}$ .

Fig. 11 presents a plot of peak area for the  $A'$  symmetry nitrobenzene modes ( $\nu_{\text{AS}}(\text{NO}_2)$  and  $\nu_s(\text{NO}_2)$ ) and the aniline-derived mode observed at 954  $\text{cm}^{-1}$  as a function of increasing temperature and indicates different binding strengths of nitrobenzene and aniline on GU-1. The  $\nu_{\text{AS}}(\text{NO}_2)$  and  $\nu_s(\text{NO}_2)$  modes of nitrobenzene remain observable in IR spectra after heating to the maximum desorption temperature (200 °C) utilised in this investigation, albeit in a significantly reduced capacity, while the aniline mode (954  $\text{cm}^{-1}$ ) is absent in the 120 °C spectrum; indicative of aniline desorption from GU-1 for the temperature range of 100–120 °C. Thus, under the stated reaction conditions, TP-IR spectra indicate nitrobenzene to have a greater binding strength to GU-1 than that of the product aniline, an outcome which is desirable for high selectivity catalysis.

The TP-IR temperature range for aniline desorption on GU-1 (100–120 °C) is illuminating. Previously in this section, we attributed adsorption of some species to the bridging hydroxyl groups of the alumina support up to a temperature of 120 °C. With the coincidence of these desorption temperatures (the absence of both the negative hydroxyl feature and the 954  $\text{cm}^{-1}$  IR feature at 120 °C), it is proposed that aniline binds to the alumina support of the catalyst *via* bridging hydroxyl groups with nitrobenzene adsorption occurring on the Pd crystallites in a vertical/tilted in the  $yz$ -plane orientation *via* monodentate binding. Furthermore, it is proposed that increasing



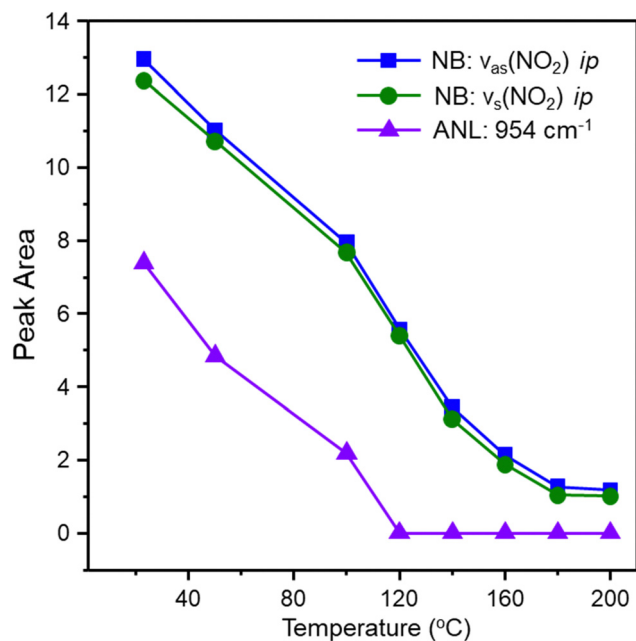


Fig. 11 Plot of peak area for nitrobenzene  $\nu_{as}(\text{NO}_2)$  and  $\nu_s(\text{NO}_2)$  modes and aniline  $\delta(\text{CH})$  at  $954 \text{ cm}^{-1}$  as observed on GU-1 as a function of increasing temperature.

nitrobenzene exposure forces the aniline that is formed from nitrobenzene hydrogenation at  $28^\circ\text{C}$  onto the support material, as indicated by the broad feature at  $954 \text{ cm}^{-1}$  in Fig. 7.

## 4. Discussion

Previous reaction testing with GU-1 revealed near complete nitrobenzene conversion, good aniline selectivity (*ca.* 90% at  $60^\circ\text{C}$ ) and a prevalence for aniline derived *vs.* nitrobenzene

derived by-products during nitrobenzene hydrogenation.<sup>8</sup> It is opportune to consider the observed catalytic behaviour with respect to the deduced adsorbate geometry and/or adsorbate location on GU-1, derived *via* DRIFTS measurements. Fig. 12 presents a schematic diagram depicting the  $C_s\sigma_v(yz)$  symmetry monodentate vertical adsorption of nitrobenzene to the Pd crystallites of GU-1; in the presence of hydrogen this produces aniline, some of which adsorbs on the support material. For higher nitrobenzene exposures, no aniline adsorbs on the Pd.

Nitrobenzene is hydrogenated to yield predominantly aniline, with low levels of by-products reported at  $60^\circ\text{C}$  (aniline derived by-products selectivity  $\leq 10\%$ ; nitrobenzene derived by-products selectivity  $\leq 0.2\%$ ).<sup>8</sup> The authors propose that it is the nitrobenzene adsorption geometry over GU-1 that is key to explaining the observed low levels of by-products associated with the reagent ( $< 0.2\%$ ). Specifically, it is the perpendicular/tilted in the  $yz$ -plane nature of the adsorption of nitrobenzene to the metal surface that results in the distancing of the aromatic moiety of the molecule to the Pd crystallites, excluding a parallel arrangement that would otherwise favour ring hydrogenation. The minimal observation of nitrobenzene derived by-products cyclohexanol and cyclohexanone, which require aromatic ring hydrogenation,<sup>9</sup> illustrate this chemical pathway to be minimised due to the proposed geometric reasons. This outcome, as observed with IR spectra, opposes those reported in Section 3.2.3. where simulated outcomes indicated a parallel adsorption of nitrobenzene over Pd(111) to be energetically favourable. However, it is crucial to re-iterate that these DFT calculations represent a single nitrobenzene molecule on a perfect Pd(111) surface – parameters of significance include (i) experimental coverages significantly exceed single molecule adsorption, and (ii) GU-1 is not a perfect Pd(111) surface. Additionally, IR measurements (Fig. 7, 9 and 10) indicate that high coverages of nitrobenzene force small quantities of aniline, formed *via* reaction with residual

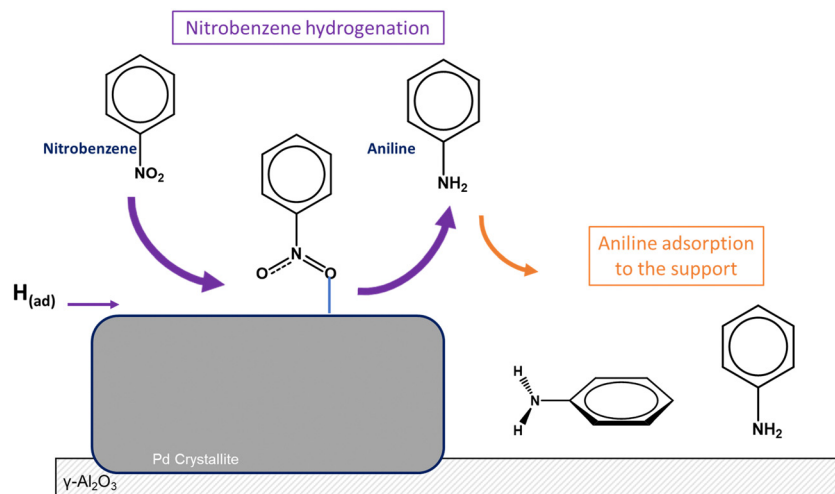


Fig. 12 Diagram visualising nitrobenzene adsorption to Pd in a vertical orientation *via* one Pd–O bond, with subsequent hydrogenation to aniline, and re-adsorption of some aniline to the support with no specific geometry identified. The solid grey box represents a non-specific Pd crystallite; the hashed box represents the  $\text{Al}_2\text{O}_3$  support. Larger arrows for vertical NB hydrogenation to ANL depicts this as the major transformation.



hydrogen, from the Pd surface onto the support material. This dynamic scenario is thought to be a contributory factor to high aniline selectivity for nitrobenzene hydrogenation over GU-1<sup>8</sup> and supported Pd catalysts in general.

## 5. Conclusions

Application of FT-IR spectroscopy, sequential nitrobenzene adsorption, TP-IR and consideration of the metal surface selection rule (MSSR) permitted determination of the adsorbate complex orientation for nitrobenzene adsorption over GU-1. The following conclusions can be drawn.

- Adsorption of nitrobenzene to GU-1 yielded DRIFTS spectra exhibiting IR features solely associated with monodentate vertical or tilted  $C_s\sigma_v(yz)$  symmetry with in-plane  $A'$  symmetry modes observed, and the IR active out-of-plane  $A''$  symmetry modes unobserved.

- Comparison of experimental outcomes and DFT simulations for a single adsorption event over Pd(111) present opposing conclusions. However, this conundrum is attributed to the DFT calculations representing single molecule adsorption to a perfect (111) surface, whereas cooperative effects at elevated coverages (exposures of  $\geq 0.93 \text{ mmol}_{(\text{NB})} \text{ g}_{(\text{cat})}^{-1}$ ), as encountered during catalytic turnover, are attributed to the nitrobenzene adopting an upright geometry.

- The lowest nitrobenzene exposure ( $0.62 \text{ mmol}_{(\text{NB})} \text{ g}_{(\text{cat})}^{-1}$ ) investigated *via* DRIFTS identified the presence of aniline on GU-1 that was formed *via* nitrobenzene reaction with residual hydrogen.

- TP-IR measurements from GU-1 indicated aniline to be interacting with bridging hydroxyl groups of the alumina support of the catalyst up to 120 °C.

- It is proposed that the vertical/tilted orientation of nitrobenzene in the  $yz$ -plane with respect to the metal surface limits the formation of nitrobenzene derived by-products due to the perpendicular positioning of the aromatic ring of the molecule with the Pd surface.

- The predominant re-adsorption of aniline to the  $\gamma\text{-Al}_2\text{O}_3$  support of GU-1 as opposed to adsorption on the Pd is proposed to limit product over-hydrogenation, and thus contributes to the elevated aniline selectivity observed.

## Data management statement

Data for this paper, including spectroscopic datasets, are available from the University of Glasgow Library *via* the following link, <http://dx.doi.org/10.5525/gla.researchdata.1447>.

## Conflicts of interest

There are no conflicts of interest to declare.

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