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Structure and properties of chiral modifiers (R)-(+)-1-(1-naphthyl)-ethylamine and (S)-(-)-1-(2-naphthyl)-ethylamine on Pd(111) using infrared spectroscopy

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ABSTRACT

(R)-(+)-1-(1-naphthyl)-ethylamine (R-1-NEA) and (S)-(-)-1-(2-naphthyl)-ethylamine (S-2-NEA) were studied on Pd(111) in ultrahigh vacuum using reflection–absorption infrared spectroscopy (RAIRS) to measure the structure, bonding and orientation using the frequency shifts and surface infrared selection rules. Temperature-programmed RAIRS experiments of NEA multilayers showed that the heat of adsorption of 2-NEA (73 kJ/mol) was>1-NEA (67 kJ/mol) resulting in 2-NEA forming ordered films when heated. Both NEA isomers adsorbed at ~ 160 K adopted flat-lying geometries at the lowest coverages with the naphthyl ring parallel to the surface with an almost vertical C-CH₃ group. However, both isomers tilted along the \times axis due to surface crowding as the first layer coverage increases and then also tilted along the y axis when the second layer was populated. Adsorption above the multilayer desorption temperatures resulted in the formation of flat-lying species for both 1-NEA and 2-NEA at all coverages.

1. Introduction

One of the most enantioselective heterogenous-phase catalysts was discovered by Orito for the platinum-catalyzed hydrogenation of α -ketoesters modified by cinchona alkaloids that can produce large enantiomeric excesses (ee) close to 100 % [1-8]. However, it has proven difficult to adsorb these modifiers onto the surfaces of model catalysts in ultrahigh vacuum (UHV) to be able to carry out fundamental investigations of the mechanisms of chirality transfer. As a result, work has instead focused on using a structural analog, 1-(1-naphthyl)-ethylamine (1-NEA), that can be efficiently and precisely adsorbed onto singlecrystal model catalysts in UHV. This molecule possesses all the requisite structural motifs of the cinchona alkaloid, namely a bicyclic ring with extended π -conjugation to facilitate surface binding [9,10] and a chiral center, in this case an ethylamine moiety at the 1-position, to act as a stereo-directing group to guide the prochiral reactant into the correct orientation. Reactants invariably interact with the organic modifier by hydrogen-bonding which are sufficiently strong to induce significant energy differences between different prochiral isomers without being so strong as to extinguish the catalytic activity altogether. The most stable prochiral structures appear to be those that simultaneously maximize the interaction between a group on the chiral center of the modifier, which in the case of NEA is an amine group, and the prochiral reactant, while still allowing it to occupy its most favorable surface adsorption site [11]. Since the stereodirecting group in cinchona alkaloids is located at the 1-position, work has focused predominantly on studying 1-naphthyl-ethylamine, while the influence of the center being located at other sites has been largely ignored [12]. However, there is no fundamental reason why the optimum location of the stereodirecting site should be the same for different modifier architectures, so that work here is also extended to studying the surface chemistry of 2-(2-naphthyl)-ethylamine (2-NEA) [13].

1-NEA has been studied previously on catalytically active platinum and palladium single-crystal surfaces in UHV [6,11,12,14-25] to generally identify flat-lying NEA structures. Vibrational studies of R-1-NEA on Pt(111) [24] used the infrared surface selection rules, in which only vibrational modes with a component normal to the surface are infrared active, [26] to identify structures in which the naphthyl plane is parallel to the surface while the C-CH₃ bond is perpendicular to it, as well as a tilted structure at low temperatures. The proposed structures were corroborated using scanning-tunneling microscopy (STM). In contrast, a tilted S-1-NEA geometry has also been identified using near-

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edge X-ray absorption fine structure (NEXAFS) experiments on a Pt (111) surface, finding a tilt angle of the naphthyl plane of $46 \pm 5^{\circ}$ with respect to the surface at 300 K [15].

STM showed that S-1-NEA is randomly adsorbed on Pt(111) at 300 K and that neither hydrogen, nor methyl pyruvate (MP), nor a combination of the two influenced NEA ordering, implying that NEA functioned through a direct one-to-one interaction with the prochiral reactant, rather than working in concert to form chiral products [27]. This was confirmed by studies of the co-adsorption of 1-NEA with MP in UHV where NEA:MP docking complexes were identified in a 1:1 ratio [15]. Heating above 320 K without co-adsorbed hydrogen induces reversible NEA dimerization through hydrogen elimination [15], while annealing to 370 K in the presence of co-adsorbed deuterium caused the irreversible elimination of the ethylamine moiety, leaving surface-bound naphthalene, coincident with enantioselectivity collapse during chiral hydrogenation [15]. STM studies of the interactions between MP and 1-NEA on Pt(111) identified docking structures and binding locations that indicated a hydrogen-bonded complex between the ester carbonyl of methyl pyruvate and the amine group of NEA [28]. Similar binding structures were observed for trifluoromethyl pyruvate and NEA using STM [29]. Finally, TPD studies of co-adsorbed MP and NEA on Pt(111) have shown that the NEA increases the thermal stability of MP [16], perhaps contributing to the rate enhancement found to accompany enantioselective hydrogenation reactions [7,28,30-41].

Studies of R-1-NEA on Pd(111) predicts that exists predominantly in an exo conformation from density functional theory (DFT) calculations and also binds to the surface through the amine group with a flat-lying naphthyl ring [20]. One-to-one docking complexes between NEA and MP have also been found on Pd(111) [11].

Studies of the interaction of methyl benzoyl formate with R-1-NEA on Pt(111) have also shown a 1:1 docking complex [42]. Trifluoromethyl pyruvate, among other compounds, have been shown to be positioned in proximity to the ethylamine group of R-1-NEA [43]. STM images of trifluoro acetophenone show the carbonyl group is directed towards the amine group, suggesting N—H····O hydrogen-bonding interactions, while steric repulsion leads to both Pro-S and Pro-R docking sites, were the Pro-S and Pro-R population correlated with the enantiomeric excess for supported catalysts [43]. The interaction between 1-NEA and other prochiral reactants show similar one-to-one interactions. Ketopantolactone on R-1-NEA and R-2-NEA modified Pt(111) have shown 1:1 docking, where the docking location was more selective with R-2-NEA than R-1-NEA [12].

The orientation and geometry of one-to-one chiral modifiers is one of the key parameters for understanding their enantioselectivity. It has been proposed that chiral modifiers with flat-lying aromatic rings promote high enantioselectivities in α -ketoester hydrogenation, while tilted structures lead to racemic products [44] as manifest by an *ee* decrease when the chiral modifier concentration exceeds an optimum value [45–47] and good correlation have been found between the concentrations at which the one-to-one modifier lays flat and those that maximize *ee* in catalysis [48–51].

Finally, the location of the ethylamine group in NEA exerts a strong influence on the intermolecular interactions so that 1-NEA is a liquid at room temperature, while 2-NEA is a solid. In view of these results, we have carried out detailed studies of 1-NEA and 2-NEA on a Pd(111) surface by RAIRS to investigate their structure and orientation as a function of coverage and temperature.

2. Materials and methods

Infrared spectra were collected using a Bruker Vertex 70 infrared spectrometer using a liquid-nitrogen-cooled, mercury cadmium telluride detector [52]. The complete light path was enclosed and purged with dry, CO₂-free air. Spectra were collected for 3000 scans at 4 cm⁻¹ resolution. Temperature-programmed reflection–absorption infrared spectroscopy (TP-RAIRS) experiments were performed by precisely

controlling the ramped sample temperature by regulating the heating current from a Kepco model ATE 6–50 M DC power supply using a homemade Labview program, which was controlled by a National Instruments card, model USB-6001 [53]. This allowed stable and accurately controllable temperature ramps to be obtained and the infrared spectra were collected continually as the temperature was varied. The sample temperature was monitored by means of a chromel/alumel thermocouple spot-welded to the edge of the single crystal, enabling the temperature to be accurately controlled and ramped at a precise rate.

The Pd(111) single crystal sample was attached to the end of a manipulator and could be resistively heated to ~ 1500 K or cooled to 80 K by thermal contact to a liquid-nitrogen-filled reservoir. The palladium was cleaned using a standard procedure consisting of cycles of argon ion sputtering and annealing in 3×10^{-8} Torr of oxygen at 1000 K as previously described [54]. The R-1-NEA (Acros, 99 % purity) and S-2-NEA (Sigma Aldrich, 99 % purity) were dosed onto the sample using the home-built Knudsen source described elsewhere [55]. The NEA dose was indicated by an exposure time in seconds or as relative coverage measured by using ¹³CO blocking experiments as described elsewhere [55].

The calculated gas-phase structure of R-1-NEA was optimized for subsequent infrared frequency calculations using Gaussian 16 using the B3LYP method and the aug-cc-pVTZ basis set. The vibrational frequencies were scaled by multiplication by a factor of 0.967 [56] and subsequently analyzed using Avogadro software to assist in the infrared assignments.

3. Results

3.1. Infrared spectroscopy of (R)-(+)-1-(1-naphthyl) ethylamine (R-1-NEA) on Pd(111)

In order to facilitate the assignments of the vibrational modes of (R)-(+)-1-(1-naphthyl) ethylamine (R-1-NEA), infrared simulations were carried out using the Gaussian 16 (G16)- optimized structure of R-1-NEA using the B3LYP functional and the aug-cc-pVTZ basis set. The results of the simulations are shown Fig. 1 (top spectrum) compared with the experimental infrared spectrum of a large multilayer of R-1-NEA adsorbed on Pd(111) at 90 K (bottom spectrum). Comparison of the peak positions from the simulations with the reported infrared spectrum of naphthalene [57] and ethylamine [58] allowed the peaks for R-1-NEA to be assigned and results are displayed in Table 1, along with the symmetries and directions of the dynamic dipole moments for each mode. The results are in good agreement with previous assignments on Pd(111) [55]. The majority of the theoretically predicted peaks are observed in the spectrum of the multilayer film with the exception of an intense feature predicted to be at 828 cm⁻¹, due to a NH₂ wagging mode. However, the presence of the 781 and 1598 cm⁻¹ amine modes indicates that the amine group is intact, consistent with previous surface studies of NEA [15]. The infrared spectra are assigned to modes either from to the ethylamine functionality (highlighted in bold in Table 1) or those due to the naphthyl ring. Note that the ethylamine group can rotate relative to the naphthyl group to form endo and exo conformers [11]. The naphthyl modes relevant to determining the bicyclic ring orientation are those at $\sim 1511~\text{cm}^{-1}$ and $\sim 1396~\text{cm}^{-1}.$ The most intense ethylamine modes are at $\sim 1598 \text{ and} \sim 781 \text{ cm}^{-1}$ due to amine vibrations and at $\sim 804 \text{ cm}^{-1}$ due to a methyl rocking mode. Note, that in the randomly adsorbed multilayer film, the mode at $\sim 804 \text{ cm}^{-1}$ is approximately 75 % of the intensity of the 781 cm⁻¹ amine mode. The chiral carbon is bound directly to the naphthyl group (at the 1 or 2 position) with a C-C bond coplanar with the ring. The methyl, amine and hydrogen are tetrahedrally displaced about the chiral carbon. Thus, surface binding of the lone pair on the amine group will lead to a CH3-C group slightly tilted away from the naphthyl group.

As a basis for selecting the appropriate conditions under which to perform experiments, and to help disentangle the effect of the



Fig. 1. Comparison of a simulated infrared spectrum of (R)-(+)-1-(1-naphthyl)-ethylamine (R-1-NEA) using Gaussian 16 with a B3LYP functional and aug-cc-pVTZ basis set, where the frequencies were scaled by a factor of 0.967 [56] (Top trace) compared with an experimental spectrum of a multilayer of R-1-NEA adsorbed on Pd (111) at 90 K.

Table 1

Assignment of the infrared spectra of (R)-(+)-1-(1-naphthyl)-ethylamine (R-1-NEA). The assignments are based on the vibrational frequencies of naphthalene and ethylamine, where group theory is used to determine the direction of the dipole enabling symmetry assignments to be made. These results are confirmed by carrying out density functional theory calculations using Gaussian 16, where the calculated frequencies are tabulated. The direction of the dynamic dipole from the calculations is shown in the last columns, using the coordinate convention shown in Fig. 3C, where the results agree with the prediction from group theory for the naphthyl rings modes. Assignments to the ethylamine group are highlighted in bold.

R-1-NEA/Pd(111)	Naphthalene	Ethylamine	Symmetry/Assignment	DFT R-1-NEA Calculation	Dipole direction from DFT
1598 (ms)	1595 (8.6)	1622	A', NH ₂ scis	1597	у
1518 (ms)	1509 (10.2)	_	-	1500	х
1447 (w)	-	1487, 1465,1455	A' CH ₃ , CH ₂ def	1448	_
1396 (w)	1389 (5.7)	1397	A' CH ₂ wag	1382	у
1365 (w)	1361 (1.9)	1378	A' CH wag	1368	Z
			$CH wag + NH_2 rock$	1320 (doublet)	_
1259 (w)	1265 (3.6)	1238, 1238	A" CH ₃ , NH ₂ tw	1245	у
1168 (m)	1144 (1.4)	_	-	1154	х
1122 (m)	1125 (2.7)	1117	A" CH ₂ rck	1100	у
924 (w)	955 (4.6)	_	-	883	Z
			NH ₂ wag	828	-
873 (m)	-	892	A' CC str	862	-
804 (s)	-	816	A" CH ₃ a-rock	798	Z
781–777 (s)	780 (127)	773	A" NH ₂ wag	766	Z

monolayer from that of the multilayer, TP-RAIRS experiments were carried out in which the sample temperature was continually varied at a rate of 0.0184 K/second while simultaneously collecting infrared spectra to provide data over small temperature intervals [53]. The temperature-dependent spectra of a large multilayer of R-1-NEA on Pd (111) are displayed in Fig. 2A indicating that modes of all symmetries start to attenuate on heating above ~ 210 K and are reduced to a constant value by ~ 224 K. Fig. 2B plots the integrated intensities of the 781

cm⁻¹ NH₂ wagging mode peak versus sample temperature. The temperature at which the multilayer desorption rate attains its maximum value is 220 K and can be considered complete by 225 K. A Redhead analysis [59] using the above heating rate and a standard pre-exponential factor of $1\times10^{13}~\text{s}^{-1}$ yields a heat of adsorption of $\sim 67~\text{kJ/mol}$, assuming that 1-NEA adsorption is not activated.

Having established the multilayer desorption temperature, exposuredependent infrared spectra were collected at selected temperatures of



Fig. 2. (A) Temperature-programmed reflection-absorption infrared spectroscopy (TP-RAIRS) experiment of a multilayer of (R)-(+)-1-(1-naphthyl)-ethylamine (R-1-NEA) adsorbed onto the Pd(111) surface at 160 K where the spectra were continually recorded while heating the sample at a linear rate of 0.0184 K/second. (B) Plot of the integrated absorbances of the 781 cm⁻¹ feature as a function of sample temperature.

90, 160 and 240 K. Experiments at 90 K result in multilayer adsorption, those at 160 K are used to compare with prior studies on Pt(111) [24], and those at 240 K specifically focus on adsorption onto only the first monolayer.

Fig. 3A displays the exposure-dependent infrared spectra of R-1-NEA

adsorbed on Pd(111) at 90 K, where multilayers of R-1-NEA will form. The relative coverages were measured using ¹³CO blocking experiments [55] in which an R-1-NEA pre-covered surface was saturated by ¹³CO to yield the infrared spectra displayed in Fig. S1A. The integrated absorbances are plotted against the R-1-NEA exposure in Fig. S1B and resulted



Fig. 3. (A) Exposure-dependent infrared spectra of (R)-(+)-1-(1-naphthyl)-ethylamine (R-1-NEA) on Pd(111) at 90 K. The relative coverages in monolayers (ML) are displayed adjacent to the corresponding spectrum. Salient peaks that are used to obtain molecular orientations are labeled. (B) Plot of the ratios of integrated intensities of 1598/782 cm⁻¹ (**E**) and 1518/782 cm⁻¹ (**E**) infrared features as a function of R-1.NEA coverage. (C) Depiction of the coordinate system used to describe the orientation of NEA on Pd(111) as a function of coverage (D) Calculated plot of the coverage of an adsorbate which has identical sticking probabilities for each layer as a function of exposure time calculated using Langmuir adsorption kinetics where the adsorption rate into each layer is taken to be proportional to the coverage of the layer below it. This is used to estimate the influence of multilayers on interpreting the infrared spectra of R-1-NEA and S-2-NEA on Pd(111) at 90 K.

in an uptake curve of coverage versus exposure shown in Fig. S1C. The results were used to establish the relative R-1-NEA coverages, which are displayed adjacent to the corresponding spectrum in Fig. 3A. The coordinate system used to describe the orientation of R-1-NEA is illustrated in Fig. 3C [60]. At the lowest sub-monolayer coverages, only the most intense peaks are detected and are assigned to a CH₃ asymmetric rocking mode (A" symmetry, which transforms as a z vector) at 791 cm⁻¹, which shifts to 804 cm^{-1} as the coverage increases, a NH₂ wagging vibration (A" symmetry, which also transforms as z) at 777 cm⁻¹ that moves to 781 cm⁻¹ as the coverage increases. As the exposure of R-1-NEA increases, additional peaks appear at 1598 cm⁻¹ and, at slightly higher coverages, at 1518 cm^{-1} , which are visible in the apparent submonolayer region. The peak at 1598 cm⁻¹ is an amine mode (which transform as a vector along the y direction) and that at 1518 cm^{-1} is a naphthyl ring mode that transforms as a vector along the x direction. The top spectrum in Fig. 3A is due to a multilayer film of R-1-NEA.

The changes in relative intensities of modes with different symmetries can be used to measure the molecular orientation. Thus, Fig. 3B plots the ratios of the integrated intensities of the 1598 (y) /781 (z) cm⁻¹ (\blacksquare) and 1518 (x)/781 (z) cm⁻¹ (\bullet) peaks as a function of coverage. As previously noted, the NEA adsorbs in a flat-laying geometry at lowest coverages. As the coverage increases to 0.3 ML and above, the mode at 1598 cm⁻¹, that transforms along the y direction, increases intensity relative to the z symmetry mode at 781 cm⁻¹ and continues to increase with larger exposures. This is evidence for a tilt along the *x*-axis, allowing modes that transform as *y* to increase in intensity due to an increase in the perpendicular component of molecules adsorbed in the first monolayer. As the coverage increases to ~ 0.6 ML, a mode that transforms as ×, centered at 1518 cm⁻¹, begins to increase in intensity compared to the 781 cm⁻¹ vibration that transforms as *z*, implying that

these higher coverages also induce ring tilting about the y axis. The exposure at which the first monolayer saturates is not clearly defined for large-molecular-weight molecules that can condense into second and subsequent layers with a high probability. To explore this, the coverage of a molecule adsorbing into the first monolayer with Langmuir adsorption kinetics was calculated but allowed for adsorption into the second and subsequent layers with the same sticking probability. The results are shown in Fig. 3D. This illustrates that molecules can adsorb into the second layer before the first monolayer has completely saturated, but the second-layer coverage is negligible for coverages below \sim 0.6 ML. It should also be noted that the amine wagging frequency at 781 cm^{-1} is identical to that for the thick film, while a shift might be expected if the amine group were bound to the substrate through the lone pair. This suggests that 1-NEA binds to Pd(111) at low coverages with the naphthyl ring parallel to the surface but with a randomly oriented ethylamine group that becomes more ordered as the coverage increases.

The change in the infrared spectrum is measured as a function of temperature to investigate how it influences the film structure and orientation. Fig. 4A displays the temperature-dependent infrared spectra of R-1-NEA on Pd(111) and was prepared by briefly heating a multilayer of R-1-NEA/Pd(111) to selected temperatures, indicated adjacent to each spectrum, and then by cooling to 90 K, at which temperature the spectra were collected. Heating to 210 K induces only slight changes to the spectra, consistent with the results in Fig. 2B, but heating to 240 K significantly attenuates the peaks because the multilayers have desorbed to leave just a monolayer behind. Now, the amine wagging mode has shifted to 777 cm⁻¹ (see Fig. 4B), suggesting that the nitrogen lone pair is now bound to the surface. It is not clear whether this had occurred during adsorption at 90 K or whether the shifted monolayer signal was obscured by 1-NEA adsorbed into the second layer where the mode



Fig. 4. (A) Temperature dependent infrared spectra of (R)-(+)-1-(1-naphthyl)-ethylamine (R-1-NEA) adsorbed on Pd(111) at 90 K and heated to various temperatures, and allowed to cool once again to 90 K, after which the spectra were recorded. The annealing temperature are displayed adjacent to the corresponding spectrum. (B) Showing a narrow scan range of the spectra shown in panel A, where identical annealing temperatures are used.

vibrates at 781 cm⁻¹. Now the 1518 cm⁻¹ naphthyl mode is absent, but the 1396 cm⁻¹ feature is detected. Since this mode transforms as a vector along the *y* direction, this implies that the naphthyl is tilted about a vector along the *x* axis. The corresponding amine scissor mode is evident (at ~ 1598 cm⁻¹) and the intense methyl modes that transform as *z* (at 1365 and 804 cm⁻¹) indicate a C-CH₃ bond that is close to normal to the surface. This suggest that 1-NEA forms a tilted structure when a crowded saturated overlayer that is formed at lower temperature is heated to allow the amine group to bind to the surface.

Heating to 270 K causes little change to the spectrum, but heating to 300 K shows a significant attenuation of the peak at 804 cm⁻¹, which still displays a 777 cm⁻¹ feature, and is a similar temperature to the onset of R-1-NEA desorption measured by TPD [19]. Heating to 350 K causes the 777 cm⁻¹ peak absorbance to reduce by \sim 50 %, which suggests the partial formation of some deprotonated, surface-bound amine, in accord with the detection of NEA dimers or trimers previously observed on platinum by STM [15]. Further heating leaves a featureless spectrum (data not shown) and is consistent with the total decomposition of R-1-NEA at temperatures above 350 K, similar to what was found previously on Pt(111) [15].

In order to investigate the influence of adsorption temperature on the structure of R-1-NEA on Pd(111), the infrared spectra were collected as a function of exposure for NEA adsorbed at 160 K for comparison with recently published literature on Pt(111) [24]. Fig. 5A shows the exposure-dependent infrared spectra of R-1-NEA/Pd(111), which is displayed over a narrower range between 750 and 850 cm⁻¹ in Fig. 5B to

highlight the frequency shifts. Again, a 777 cm^{-1} peak is detected at lower exposures than those at which the 804 $\rm cm^{-1}$ feature is seen. This suggests a structural transition within the first monolayer when the interaction between the naphthyl ring and the surface is strong enough to attenuate the infrared signal from the A" CH₃ asymmetric rocking modes at the lowest coverages. Fig. 5C plots the integrated absorbances of the 777–781 cm^{-1} peaks as a function of exposure. Their intensities increase almost linearly for exposures between 8 and 12 s, but decrease at \sim 17 sec exposure, increasing once again as the exposure increases further. This is accompanied by a shift in frequency from 777 (■) to (■) 781 cm^{-1} . According to the surface selection rules [26] the apparent intensity decrease of a mode with *z* symmetry with increasing coverage suggests that it is due to molecular tilting, which is reinforced by detecting the accompanying peak that transforms as y at 1598 cm^{-1} indicating tilting along the \times axis at submonolayer coverages. At higher exposures, a mode at 1511 cm^{-1} appears, indicating the growth of a randomly oriented second layer.

Fig. 6 show the exposure-dependent infrared spectra of R-1-NEA/Pd (111) adsorbed at 240 K, a temperature at which the multilayer has desorbed (Fig. 2B). Now the low-frequency amine wagging mode appears at 777 cm⁻¹ confirming that the shift is due to an amine binding via its lone pair electrons to the surface. The saturation of the first monolayer is confirmed by the change in intensity of the 777 cm⁻¹ peak as a function of exposure time (Fig. 6B), which saturates after a \sim 35 s exposure. No naphthyl ring peaks at 1598 cm⁻¹ (that transforms as *y*) or



Fig. 5. (A) Exposure-dependent infrared spectra of (R)-(+)-1-(1-naphthyl)ethylamine (R-1-NEA) on Pd(111) at 190 K that emphasize the range between 750 and 850 cm⁻¹. The exposures (in seconds) are displayed adjacent to the corresponding spectrum. (B) Plot of the Integrated absorbances of 781 cm⁻¹ peak as a function of exposure time in seconds.



Fig. 6. (A) Exposure-dependent IR spectra of (R)-(+)-1-(1-naphthyl)-ethylamine (R-1-NEA) on Pd(111) at 240 K. The exposures (in seconds) are displayed adjacent to the corresponding spectrum. (B) Plot of the Integrated absorbances of that 777 $\rm cm^{-1}$ peak as a function of exposure time in seconds.

at 1518 cm⁻¹ (that transforms as *y*) are detected, indicating that the plane of the naphthyl ring lies flat. Again, the presence of the 1365 and 797 cm⁻¹ modes indicated that the C-CH₃ bond is close to perpendicular to the surface. This assignment is illustrated in greater detail in Figure S2, where monolayer (top) spectrum of R-1-NEA is compared with the multilayer spectrum at the bottom. To facilitate comparison, the multilayer signals were scaled to yield similar intensities to those found in the monolayer spectrum. The most notable difference between the randomly adsorbed multilayer and the monolayer 1-NEA formed at 240 K is that the modes with *x* (at 1518 cm⁻¹) and *y* symmetries (at 1396 cm⁻¹) are clearly absent from the spectrum of the monolayer formed at 240 K, confirming that the naphthyl plane is parallel to the surface.

3.2. Infrared spectroscopy of (S)-(-)-1-(2-Naphthyl)-Ethylamine (S-2-NEA) on Pd(111)

Based on the results for R-1-NEA on Pd(111), experiments were carried out to investigate the effect of moving the ethylamine group to the 2-position on the naphthyl ring by studying S-(2-naphthyl)-ethyl-amine (2-NEA) [13]. As indicated in Table 2, the assignments of the vibrational modes for both NEA isomers are essentially identical, although minor differences do arise. For example, the location of the ethylamine group shifts the NH₂ wagging mode frequency from ~ 781 cm⁻¹ when at the 1 position to ~ 750 cm⁻¹ when bound at the 2 position.

In order to establish the appropriate temperatures to carry out more detailed experiments and to determine multilayer desorption temperature, a series of TP-RAIRS experiments were carried out for a multilayer of S-2-NEA on Pd(111) and the results are displayed in Fig. 7A and are very different for those for R-1-NEA (Fig. 2A). The major difference is a large intensity increase of all modes on heating to ~ 215 K, which is accompanied by the peaks becoming narrower. However, the intensities do not increase equally for modes of all symmetries as illustrated in Fig. 7B. Here, the 895 cm⁻¹ peak (NH₂ wag) shows a large increase in integrated absorbance, while the change for the 750 cm⁻¹ peak shows only a slight decrease. The spectra are compared in Fig. 8, which displays the spectrum of S-2-NEA adsorbed onto Pd(111) at 90 K compared with the spectrum found after heating to 223 K. To aid in visual comparison, the signal of the sample heated to 223 K was attenuated so that

Table 2

Assignment of the infrared specra of (S)-(+)-1-(2-naphthyl)-ethylamine (S-2-NEA). The assignments are based on the vibrational frequencies of naphthalene and ethylamine shown in Table 1, where group theory is used to determine the direction of the dipole enabling symmetry assignments to be made. These results are confirmed by carrying out density functional theory calculations using Gaussian 16, where the calculated frequencies are tabulated. The direction of the dynamic dipole from the calculations is shown in the last columns, using the coordinate convention shown in Fig. 3C, where the results agree with the prediction from group theory for the naphthyl rings modes. Assignments to the ethylamine group are highlighted in bold.

Vibrational Frequencies/cm ⁻¹					
S-2-NEA/Pd(111)	Symmetry/Assignment	Dynamic dipole direction from DFT			
1601 (ms)	A', NH ₂ scis	у			
1508 (ms)	-	х			
1450 (w)	A' CH ₃ , CH ₂ def	-			
1382 (w)	A' CH ₂ wag	у			
1372 (w)	A' CH wag	Z			
	CH wag + NH ₂ rock	_			
1270 (w)	A" CH ₃ , NH ₂ tw	у			
1174 (m)	-	x			
1126 (m)	A" CH ₂ rck	у			
927 (w)	-	Z			
895 (m)	NH_2 wag	_			
860-854 (m)	A' CC str	_			
816-823 (s)	A" CH ₃ a-rk	Z			
750–744 (s)	A" NH ₂ wag	Z			

the 754-cm⁻¹ peak in the 223-K spectrum was approximately equal in intensity to the 750-cm⁻¹ peak in the 90-K spectrum. Several peaks shift slightly on annealing the film from 90 to 223 K [53], but the most significant changes are the appearance of peaks at 1027, 1174 and 1304 cm⁻¹ that are either very weak or non-existent in low-temperature spectrum.

These changes connote a large structural change of the film prior to multilayer desorption at ~ 245 K that is not seen for R-1-NEA that implies stronger intermolecular interactions either due to π - π stacking or to the coupling of aligned dipoles [53]. The sublimation activation energy can again be gauged using a Redhead analysis [59] from the temperature of 250 K at which multilayer desorption rate is maximum to yield a value of ~ 73 kJ/mol. This is larger than for 1-NEA and confirms that there are stronger intermolecular interactions for S-2-NEA than for R-1-NEA. This is in accord with the observation that S-2-NEA is a solid at room temperature while R-1-NEA is a liquid, and that ordered films form from 2-NEA, but not from 1-NEA.

Again, these experiments define the appropriate adsorption temperatures so that infrared spectra were collected for (S)-(-)-1-(2-naphthyl)-ethylamine (S-2-NEA) at 160 K, where it can adsorb into the second and subsequent layers, and at 245 K, where it adsorbs only on the surface. Fig. 9A shows the exposure-dependent infrared spectra of S-2-NEA/Pd(111) adsorbed on Pd(111) at 160 K, where the 2-NEA coverages are indicated adjacent to the corresponding spectra. At the lowest coverages, below ~ 0.2 ML, only peaks appear at 744 cm⁻¹ (NH₂ wag) and 816 cm^{-1} (methyl rocking mode) that transform as *z* (see Table 2), but no peaks due to the naphthyl ring (at 1508 and 1382 cm^{-1}) are evident indicating that, similar to 1-NEA, the naphthyl ring lies parallel to the surface with an almost perpendicular C-CH₃ bond with an amine bound to the surface via its lone pair of electrons. As the coverage increases to ~ 0.48 ML, the mode that transforms as y, centered at 1601 cm⁻¹, increases in intensity to indicate the presence of a tilted species at low temperatures for submonolayer coverages.

As the coverage increases above ~ 0.6 ML, a naphthyl mode at 1508 cm⁻¹ that transforms as *x* (Fig. 9B) grows with increasing coverage, suggesting that the 2-NEA starts to tilt about its y axis as well, similar to the behavior of 1-NEA, at the onset of the second-layer growth. This is accompanied by an increase in intensity of the 1382 cm⁻¹ peak due to the naphthyl ring that transforms as *x* suggesting that the naphthyl plane tilts so that both the *x* and *y* vectors of the adsorbed molecule have components perpendicular to the surface and is possibly due to a randomly oriented second-layer. This is confirmed by the shift in NH₂ bending frequency from 744 cm⁻¹ at the lowest coverage to 750 cm⁻¹ for the multilayer similar to the shift from 781 to 777 cm⁻¹ for 1-NEA on Pd(111).

The exposure-dependent infrared spectra of a S-2-NEA monolayer adsorbed on Pd(111) at 245 K are shown in Fig. 10. They exhibit several peaks that transform as *z* at 854 (C—C stretch), 816 (CH₃ asymmetric rocking mode) and 744 cm⁻¹ (NH₂ wagging mode) (see Table 2). However, no peaks due to the naphthyl ring, that would appear at ~ 1508 and 1382 cm⁻¹ are detected. This implies that the naphthyl group in the S-2-NEA monolayer lies parallel to the surface and that no tilting is detected when it adsorbs directly on the surface. The amine vibration at 744 cm⁻¹ indicates that the nitrogen lone pair electrons are donated to the Pd(111) substrate, and the ethyl group vibrations indicate that the C—C axis is close to perpendicular to the surface in a room-temperature structure that is similar to that found for 1-NEA on Pd(111).

Fig. 11 shows the temperature-dependent infrared spectra of a saturated S-2-NEA/Pd(111) monolayer adsorbed at 245 K. The spectra do not change significantly upon annealing to 265 K, but peaks at 854, 816 and 744 cm⁻¹ attenuate slightly on heating to 300 K. At 350 and 400 K, the peak at 854 cm⁻¹ peak disappears leaving only features at 816 and 744 cm⁻¹. Annealing to 450 K causes a slight shift in the 816 cm⁻¹ peak and the growth of a new feature at 775 cm⁻¹ that is accompanied by the disappearance of the 1369 cm⁻¹ mode.



Fig. 7. Temperature-programmed reflection-absorption infrared spectroscopy (TP-RAIRS) experiment of a multilayer of (S)-(-)-1-(2-naphthyl)-ethylamine (S-2-NEA) adsorbed onto the Pd(111) surface at 160 K where the spectra were continually recorded while heating the sample at a linear rate of 0.0184 K/second. (B) Plots of the integrated absorbances of the 750 (\blacksquare) and 895 (\bullet) cm⁻¹ features as a function of sample temperature.



Fig. 8. Comparison of the infrared spectra of a (S)-(-)-1-(2-naphthyl)-ethylamine (S-2-NEA) multilayer film adsorbed onto Pd(111) at 90 K (Bottom spectrum) and after annealing to 223 K (Top spectrum). The Absorbance scales have been adjusted so that the peak heights are similar.

4. Discussion

The infrared results show that the structure and orientation of R-1-NEA and S-2-NEA on Pd(111) depend both on the coverage and the temperature. Initial TP-RAIRS experiments were carried out to determine the multilayer desorption temperatures to establish the conditions for more detailed experiments of the structure and surface chemistry of NEA. These temperature-programmed experiments enable the activation energies of sublimation of multilayer films on palladium to be measured by assuming a standard pre-exponential factor of $1\times10^{13}\,s^{-1}$ and yielded values of \sim 67 kJ/mol for 1-NEA and \sim 73 kJ/mol for 2-NEA. If it is assumed that molecular adsorption is not activated, these values correspond to the heat of adsorption from the gas phase, but the absolute value will depend (weakly) on the choice of pre-exponential factor, while their relative values will be valid. This indicates that the intermolecular interactions depend strongly on the location of the eth-ylamine group. This is also manifest by a higher melting point of 2-NEA than 1-NEA and the significant enhancement in infrared signals due to



Fig. 9. (A) Exposure-dependent infrared spectra of (S)-(-)-1-(2-naphthyl)-ethylamine (S-2-NEA) on Pd(111) at 160 K. The relative coverages in monolayers (ML) are displayed adjacent to the corresponding spectrum. Salient peaks that are used to obtain molecular orientations are labeled. (B) Plot of the integrated intensities of the peaks at 750 (\checkmark), 824 (\blacktriangle), 1601 (\bigcirc) and 1508 (\blacksquare) cm⁻¹ as a function of the coverage in ML.

the film ordering by annealing a random film deposited into Pd(111) at \sim 110 K (Fig. 7).

Based on these results, the R-1-NEA and S-2-NEA were adsorbed onto Pd(111) at 90 or 160 K, where higher exposure leads to the formation of a multilayer. The structures and molecular orientations were analyzed using the surface selection rules [26]. Naphthyl-ethylamine consists of a rigid naphthyl species attached to a chiral ethylamine center via a single C-C bond that allows the chiral group to rotate relative to the planar naphthyl species so that it can exist in either the endo or exo conformer. The vibrational frequencies are assigned by comparing the NEA spectra with those for naphthalene [57] and ethylamine [58] complemented by DFT calculations (Tables 1 and 2). Infrared features could then be associated with the naphthyl group or the chiral center to enable their individual orientations to be established. Note that it has been found previously that the stable structures formed at room temperature on Pd (111) are controlled by the preferred amine binding site that causes the naphthyl ring to be translated to a less stable site than that preferred by naphthalene alone [11].

The general features of the chemistry of both chiral modifiers are similar but there are key differences. Both 1-NEA and 2-NEA adsorb at low temperature, below the multilayer desorption temperature, with the naphthyl group parallel to the surface for coverage below ~ 0.2 monolayer. At 90 K, the ethylamine group appears to be randomly oriented with respect to the bicyclic ring and begins to order as the temperature increases. For higher coverages at low temperatures, surface crowding induces molecular tilt, that has, for example, been seen previously for benzene on Pd(111) [61]. In the case of 1-NEA on Pd(111), the tilt occurs by rotation about the \times axis (Fig. 3). Similar observations have been made for 1-NEA/Pt(111) [24] by combining infrared measurements with STM imaging, which revealed a similar tilting of submonolayer coverages of 1-NEA where it tilts about the x-axis when adsorbed at 160 K. Inspection of the published STM images of 1-NEA adsorbed at 160 and 300 K in that work provides insights into the mechanism of this low-temperature tilting, which is not observed at temperatures above 240 K. Thermodynamically, the system will adjust to minimize the total energy. When the adsorbate coverage is low, planar, π -conjugated molecules such as benzene [61,62] and naphthalene [9] will bind with the molecular plane parallel to the surface to maximize the π -orbital-surface interaction. However, as the surface coverage increases, additional molecules can be accommodated by tilting as long as this energy lost by an adsorbate partially decoordinating from the surface is compensated by the resulting increased intermolecular interactions. The radial distribution functions from STM images of 1-NEA/Pd(111) shows no order at either low or high coverages at 300 K [19]. Thus, the interaction energies that induce NEA tilting at 160 K are not sufficiently strong to induce tilting at the elevated temperatures needed for catalytic hydrogenation reactions.

The structures formed by both NEA isomers at temperatures at which the second layer cannot form are similar and in agreement with previously proposed room-temperature structures relevant to the conditions used for chiral catalysis [11]. Here the naphthyl group lies parallel to the surface with an almost vertical C-CH₃ group that enables the amine lone pair electrons to bind to the substrate for both 1-NEA and 2-NEA. Note that chirality transfer to methyl pyruvate occurs via it being bound such that it can hydrogen-bond to the amine group while adsorbing on a stable site on the substrate and so is also influenced by the location of the stereodirecting group [11].

Both chiral modifiers are stable at room temperature (Figs. 4 and 11), requiring the catalyst to be active at this temperature. Alkyl groups on palladium and platinum decompose via β -hydride elimination [63–65] but the methyl deformation vibration remains intact up to ~ 400 K for both 1- and 2-NEA suggesting that dehydrogenation take place preferentially either on the amine group or by α –C–H bond scission. However, for both isomers, the most-intense amine wagging modes (at 777 cm⁻¹ for 1-NEA and 744 cm⁻¹ for 2-NEA on Pd(111)) remain intact to quite high temperatures and are still evident at 400 K for 2-NEA (Fig. 11) and 350 K for 1-NEA (Fig. 4). As the 1-NEA is heated to 350 K, the amine mode at 777 cm⁻¹ decreases intensity and this observation is in agreement with the possible deprotonation of the chiral center suggested by STM images of 1-NEA on Pt(111) which show the reversible dimer formation on heating to 320 K [15].

5. Conclusion

The structures and stability of NEA chiral modifiers are central to understanding heterogenous-phase chirality transfer and is studied here using reflection–absorption infrared spectroscopy, where the shifts in vibrational frequencies indicates changes in molecular structure, and the surface selection rules provide information on the adsorbate structure, in particular, by using vibrational frequencies that can be assigned specifically to the naphthyl or ethylamine moieties of NEA to gauge the orientations of different portions of the molecule to obtain a detailed structural picture. Experiments were carried out for the two isomers, 1-NEA and 2-NEA, to investigate how the location of the stereodirecting ethylamine group influences the adsorption structure.

The structures of 1-NEA and 2-NEA on Pd(111) as a function of coverage are relatively similar. They form flat-lying species at lowest



Fig. 10.) Exposure-dependent infrared spectra of (S)-(-)-1-(2-naphthyl)-ethylamine (S-2-NEA) on Pd(111) at 245 K. The exposures (in seconds) are displayed adjacent to the corresponding spectrum.



Fig. 11. Temperature dependent infrared spectra of (S)-(-)-1-(2-naphthyl)ethylamine (S-2-NEA) adsorbed on Pd(111) at 245 K and heated to various temperatures, and allowed to cool once again to 245 K, after which the spectra were recorded. The annealing temperature are displayed adjacent to the corresponding spectrum.

submonolayer coverages at ~ 160 K and below, while tilting away from surface along the \times axis as the first layer becomes crowded and along the *y* axis as the second layer growth begins. Similar tilting behavior is seen for 1-NEA on platinum. The 1-NEA and 2-NEA form flat-laying species at all coverages above the multilayer desorption temperatures, of > 225 K for 1-NEA and > 245 K for 2-NEA.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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