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# Enantiospecific equilibrium adsorption and chemistry of D-/L-proline mixtures on chiral and achiral Cu surfaces

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#### Abstract

A fundamental understanding of the enantiospecific interactions between chiral adsorbates and understanding of their interactions with chiral surfaces is key to unlocking the origins of enantiospecific surface chemistry. Herein, the adsorption and decomposition of the amino acid proline (Pro) have been studied on the achiral Cu(110) and Cu(111) surfaces and on the chiral Cu(643)<sup>R&S</sup> surfaces. Isotopically labelled 1-<sup>13</sup>C-L-Pro has been used to probe the Pro decomposition mechanism and to allow mass spectrometric discrimination of D-Pro and 1-<sup>13</sup>C-L-Pro when adsorbed as mixtures. On the Cu(111) surface, X-ray photoelectron spectroscopy reveals that Pro adsorbs as an anionic species in the monolayer. On the chiral  $Cu(643)^{R\&S}$  surface, adsorbed Pro enantiomers decompose with non-enantiospecific kinetics. However, the decomposition kinetics were found to be different on the terraces versus the kinked steps. Exposure of the chiral Cu(643)<sup>*R&S*</sup> surfaces to a racemic gas phase mixture of D-Pro and 1-<sup>13</sup>C-L-Pro resulted in the adsorption of a racemic mixture; i.e., adsorption is not enantiospecific. However, exposure to non-racemic mixtures of D-Pro and 1-<sup>13</sup>C-L-Pro resulted in amplification of enantiomeric excess on the surface, indicative of homochiral aggregation of adsorbed Pro. During coadsorption, this amplification is observed even at very low coverages, quite distinct from the behavior of other amino acids, which begin to exhibit homochiral aggregation only after reaching monolayer coverages. The equilibrium adsorption of D-Pro and 1-13C-L-Pro mixtures on achiral Cu(110) did not display any aggregation, consistent with prior scanning tunneling microscopy (STM) observations of DL-Pro/Cu(110). This demonstrates convergence between findings from equilibrium adsorption methods and STM experiments and corroborates formation of a 2D random solid solution.

#### **KEYWORDS**

adsorption, amino acid, chiral, copper, enantioselective, proline, surface

# **1** | INTRODUCTION

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Chirality is the geometrical property of molecules (and objects in general) wherein the mirror image of the molecule is not superimposable onto itself. The two mirror

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images are called enantiomers, and their handedness is denoted by various conventions as D-/L- or R-/S-.<sup>1</sup> This disymmetry manifests itself in biological/chemical processes, necessitating a deeper understanding of chiral chemistry. The most prominent manifestation of the

importance of chirality is the homochirality of life; biomolecules such as DNA and amino acids that are the molecular building blocks of life on Earth are present only in one enantiomeric form in nature.<sup>2</sup> As a consequence, many artificial chiral compounds such as pharmaceuticals and agrochemicals with bioactive functions must be produced in enantiomerically pure form. This necessitates the development of enantioselective chemical processes. In recent years, much research has focused on the adsorption and reaction of chiral molecules on chiral surfaces relevant to applications in the fields of heterogeneous catalysis,<sup>3,4</sup> chromatographic separation of enantiomers,<sup>5-7</sup> supramolecular self-assembled systems,<sup>8,9</sup> and materials such as liquid crystals<sup>10</sup> and sensors.<sup>11,12</sup> Specifically, the interaction of natural amino acids (all but one of which are chiral) with surfaces has been studied in recent years because amino acids serve as model systems for understanding the interactions of large biomolecules, such as proteins, with surfaces.<sup>13-16</sup>

One of the key questions regarding chiral adsorbates on surfaces is whether mixtures of adsorbed enantiomers separate homochirally into conglomerates (enantiomerically pure domains) or heterochirally into racemates (domains containing equimolar mixtures of enantiomers).<sup>17,18</sup> In 3D, racemic mixtures of chiral molecules crystallize overwhelmingly as racemates (approximately 90%), while the remainder are conglomerates.<sup>19</sup> Whether the same is true in 2D remains unanswered. A long-standing hypothesis suggests that chiral molecules should assemble preferentially as conglomerates because symmetry elements that are typical of racemate structures in 3D (inversion and twofold screw axes) cannot exist at asymmetric interfaces.<sup>18</sup> A recent review of all relevant scanning tunneling microscopy (STM) images of adsorbed racemic mixtures paints a complex picture of their aggregation. Both homochiral and heterochiral assemblies are observed but without evidence of either one being preferred over the other.<sup>15</sup> That review revealed that homochiral versus heterochiral aggregation is not only dependent on adsorbate and surface structures but also dependent on parameters such as surface coverage, surface temperature, and enantiomeric excess in the adsorbed monolayer. Thus, a model that is based only on the symmetry elements found in 2D and 3D may not be sufficient to capture the complexity of enantiomer aggregation on surfaces.

In this paper, we discuss the aggregation and decomposition of the chiral amino acid proline (Pro) on single crystal Cu surfaces. Pro is one of the 20 naturally occurring  $\alpha$ -amino acids. It consists of a carboxylate group bonded to a heterocycle ring with an imino group (Figure 1). Pro is unique among the naturally occurring amino acids because it is the only one in which the *N*- atom is part of a heterocyclic ring. In all other amino acids, the  $C_{\alpha}$  is tetrahedrally bonded to a carboxylate group, an amino group, a functional group, and a hydrogen atom. Of all the naturally occurring  $\alpha$ -amino acids, Pro is also the most structurally rigid. The most stable form of the Pro molecule has both the carboxylic acid group and the N—H bond on the same side of the heterocycle ring.<sup>20,21</sup> This rigidity influences the bonding and orientation of Pro enantiomers adsorbed on surfaces, enabling visual identification and enantiodifferentiation of Pro enantiomers on Cu(110) using STM.<sup>22,23</sup>

The Cu surfaces used in this study are the naturally chiral Cu(643)<sup>R&S</sup> surfaces and the achiral Cu(110) and Cu(111) surfaces. The idealized structures of these surfaces are shown in Figure 1. In addition to the chiral Cu(643)<sup>*R&S*</sup> surfaces, the Cu(110) surface has been studied to forge a connection between the results of our methods and the previously mentioned STM results.<sup>23</sup> The Cu(111) surface has been studied because it has the same structure as the terraces of the chiral  $Cu(643)^{R\&S}$ surfaces and is the closest low Miller index plane in surface orientation space. Naturally chiral surfaces typically have structures based on low Miller index terraces separated by monoatomic steps that are formed of low Miller index step edges interrupted by kinks.<sup>24</sup> The chiral crystal planes are oriented such that none of the bulk mirror planes lie perpendicular to the surface. Naturally chiral surfaces have been used in the recent past to study enantiospecific phenomena such as adsorption energetics, reaction kinetics, adsorbate orientation, enantiomer separations, and enantiomer aggregation.<sup>25-30</sup>

The rigidity of Pro has been employed in metalcatalyzed diastereoselective hydrogenation reactions to produce enantiopure hydrogenated products.<sup>31-34</sup> In these reaction schemes, Pro is used as a chiral auxiliary that forms an intermediate compound with the organic reactant. Given the rigidity and chirality of Pro, this intermediate then adsorbs on the metal catalyst surface in single enantiomer conformation which in turn causes the hydrogenation reaction to yield an enantiomeric excess in the organic product.

Given these interesting observations, Pro adsorption and surface chemistry has been studied extensively by a number of researchers.<sup>35-39</sup> Tysoe et al studied the adsorption and decomposition of L-Pro on Pd(111) using temperature-programmed reaction spectroscopy (TPRS) and X-ray photoemission spectroscopy (XPS). They found that Pro on Pd(111) is adsorbed as a zwitterion in the monolayer and decomposes via a complex pathway, starting with the dissociation of the  $C_{\alpha}$ —COO bond to form CO<sub>2</sub> and pyrrolidine, (CH<sub>2</sub>)<sub>4</sub>NH, which in turn dehydrogenates to pyrrole (C<sub>4</sub>H<sub>4</sub>NH), HCN, and other nitrile compounds, detected by mass spectrometry as a <sup>202</sup> WILEY





Cu(110)

Cu(111)

Cu(643)<sup>s</sup>

**FIGURE 1** The molecular structure of L-Pro with the carbon atoms of the heterocyclic ring labelled  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ .  $C_{\alpha}$  is the chiral center with the relative orientation of the hydrogen atom and the –COOH group determining the chirality. The carboxylic group carbon, marked with (\*), is isotopically labelled in 1-<sup>13</sup>C-L-Pro to distinguish it from D-Pro in mass spectrometry measurements. Structures of the chiral Cu(643)<sup>*S*</sup>, achiral Cu(110), and achiral Cu(111) surfaces. The kinks on Cu(643)<sup>*S*</sup> break surface symmetry

complex mixture.<sup>36,40</sup> L-Pro modified surfaces have been shown to exhibit weak enantioselectivity for chiral 2butanol (CH<sub>3</sub>CH(OH)CH<sub>2</sub>CH<sub>3</sub>) adsorption, yielding a ratio of *S*- to *R*-2-butanol of 1.2.

Madden et al studied structural phases formed when Pro is adsorbed on Cu(311). They found that Pro adsorbs in the anionic form on the Cu(311) surface, with a transition from  $\mu_3$  bonding (with the two carboxylate oxygen atoms and the nitrogen atom participating in binding to the surface) at low coverages to a mixture of  $\mu_3$  bonding and  $\mu_2$  bonding through the carboxylate group at higher coverages. After adsorption and subsequent annealing to 350 into 420 K, the pyrrolidine ring dehydrogenates, and hydrogen is evolved, as indicated by reflection absorption infrared spectroscopy (RAIRS) and confirmed by TPRS.<sup>38</sup> At temperatures of 460 to 480 K, the carboxylate group dissociates from the dehydrogenated ring and desorbs from the surface as  $CO_2$  with the dehydrogenated ring desorbing as pyrolle at slightly higher temperatures.

The adsorption of enantiopure and racemic Pro on Cu(110) has also been studied using STM, RAIRS, and low-energy electron diffraction (LEED).<sup>23,37,41</sup> On Cu(110), racemic Pro adsorbs in an anionic form in the monolayer. The key observation was that each enantiomer of Pro adsorbs in two different conformations. Both molecular chirality and adsorption chirality (the latter because of the two adsorption conformations of each enantiomer) are observed. In other words, the four conformations of adsorbed Pro/Cu(110) (two for each enantiomer) arise from the fact that it forms diastereomers

on the surface. Raval et al introduced the concept of handedness and footedness, respectively, to distinguish between the two chiral centers arising from a chiral molecule adsorbed on a surface. The four conformations are  $R_{\rm h}R_{\rm f} \equiv S_{\rm h}S_{\rm f} \not\equiv R_{\rm h}S_{\rm f} \equiv S_{\rm h}R_{\rm f}$  where R and S refer to the chirality arising from both handedness (h, molecular chirality) and footedness (f, adsorption footprint).<sup>37</sup> Further, both D- and L-Pro molecular enantiomers were found to be present in the same domain, revealing heterochiral aggregation rather than homochiral aggregation. Interestingly, the mixture of D- and L-Pro enantiomers is randomly ordered, something that is only rarely observed in 3D racemates. It bears reiteration that observation of this type of molecular-level detail is possible only because the enantiomers of Pro on Cu(110) adsorb in enantiomorphous conformations with sufficiently high STM contrast to be visually distinguished.

In this paper, the decomposition and enantiospecific aggregation of Pro on achiral Cu(111), achiral Cu(110), and chiral Cu(643)<sup>*R&S*</sup> are discussed. The decomposition of Pro on Cu(111) was compared with the decomposition on  $Cu(643)^{R\&S}$ , as the latter is composed of (111) terraces, and the comparison decouples the influence of the terrace from that of steps and kinks on Pro decomposition. Cu(110) was also studied because enantiomer aggregation has been studied in the Pro/Cu(110) system using STM.<sup>23</sup> This work seeks to corroborate the STM observation that there is no apparent enantiospecific aggregation of DL-Pro on Cu(110) into either ordered conglomerate or racemate domains. First, we discuss XP spectra of Pro/Cu(111) that reveal Pro to be adsorbed as a zwitterion in the multilaver and as an anion in the monolayer. Next, we discuss the mechanism and kinetics of Pro decomposition on Cu(643)<sup>*R&S*</sup>, as determined by isotopic labelling. While no evidence of enantiospecific decomposition was found for Pro/Cu(643)<sup>R&S</sup>, Pro was found to decompose at different temperatures on the steps and the terraces of Cu(643)<sup>R&S</sup>. Lastly, equilibrium adsorption of D- and L-Pro mixtures on Cu(643)<sup>*R&S*</sup> reveal homochiral aggregation but without enantiospecific adsorption on Cu(643)-R&S. In contrast, there are no signs of enantiospecific aggregation during equilibrium adsorption of D- and L-Pro mixtures on Cu(110).

#### 2 | MATERIALS AND METHODS

TPRS and equilibrium adsorption experiments for Pro/Cu(643)<sup>*R&S*</sup> and Pro/Cu(110) were performed in an ultrahigh vacuum (UHV) chamber operating at a base pressure of  $10^{-9}$  Torr. The UHV chamber is equipped with a (*x*, *y*, *z*,  $\theta$ ) manipulator used to position the crystal in the chamber, an Ar<sup>+</sup> sputter ion gun to clean the

surface, and a LEED optics to verify the surface orientation. D- and L-Pro were sublimated onto the  $Cu(643)^{R\&S}$ and Cu(110) surfaces from powders using a Kentax two cell organic evaporator. Finally, an Extrel quadrupole mass spectrometer was used to detect gas phase species being introduced into the chamber and species desorbing from the surface.

The Cu(643)<sup>R&S</sup> and Cu(110) crystals (Monocrystals Company, Ohio) are 10 mm in diameter by 2 mm thick and spot welded to Ta wires at the end of the manipulator. The single crystal exposes the  $Cu(643)^R$  surface on one side and its enantiomer,  $Cu(643)^S$ , on the opposite side. A K-type chromel-alumel thermocouple was spot welded onto the edge of the crystal for temperature measurement. Using liquid nitrogen, the crystal could be cooled to 90 K and heated resistively to 1,000 K. The crystal was cleaned by multiple sputter/anneal cycles consisting of sputtering with Ar at  $5 \times 10^{-5}$  Torr and an  $Ar^+$  energy of 1 keV. While being sputtered, the crystal was held at 850 K followed by annealing at 900 K. In addition to using electron backscatter diffraction to verify the crystal surface orientation, LEED was used after sputter/anneal cycles to verify the long-range order and chirality of the surface.

Unlabelled D-Pro (Sigma Aldrich, 99 atom%), 1-<sup>13</sup>C-L-Pro (Cambridge Isotope Laboratories, 99 atom%), and <sup>15</sup>N,1-<sup>13</sup>C-L-Pro (Cambridge Isotope Laboratories, 99 atom%) were used for the experiments. The D- and L-Pro were loaded into two resistively heated quartz crucibles in the Kentax evaporator. The temperatures of the vials were controlled independently at 330 to 345 K to achieve sublimation of Pro vapor onto the crystal. The vials were positioned 2.5" from the crystal to achieve uniform coverage,  $\theta$ , across the surface. During heating, the decomposition of the adsorbed Pro yields gas phase H<sub>2</sub>, CO<sub>2</sub>, and pyrrole (C<sub>4</sub>H<sub>4</sub>NH). CO<sub>2</sub> from 1-<sup>13</sup>C-L-Pro is detected at m/z = 44, while <sup>13</sup>CO<sub>2</sub> from 1-<sup>13</sup>C-L-Pro is detected at m/z = 45, allowing quantitative measurement of the relative coverages of D- and L-Pro on the surface.

The TPRS experiments were conducted by sublimating D-Pro or 1-<sup>13</sup>C-L-Pro (placed in separate vials in the Kentax evaporator) onto the single crystal surfaces. The duration of the surface exposure to the Pro fluxes was controlled by opening/closing a shutter placed in front of the vials while holding the crystal at a constant temperature of 400 K. This surface temperature was high enough to prevent multilayer formation while also allowing acceptable rates of displacement between adsorbed and gas phase Pro. After Pro adsorption, the crystal was moved in front of the mass spectrometer, and TPRS was conducted by heating the surface at a constant rate of 2 K/s while monitoring the desorption of decomposition products. The coverage of D-Pro was

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estimated by measuring the area under the TPRS peak at m/z = 44 and normalizing by its maximum area (obtained at monolayer coverage). The coverage of 1-<sup>13</sup>C-L-Pro was estimated similarly.

Equilibrium adsorption experiments were conducted on the Cu(643)<sup>*R&S*</sup> and the Cu(110) surfaces by simultaneously sublimating both D-Pro and 1-<sup>13</sup>C-L-Pro from two separate vials at constant fluxes and a given D-/L-Pro ratio,  $P_D/P_L$ , for various exposure times. The D-/L- coverage ratio,  $\theta_D/\theta_L$ , on the surface after each exposure was determined by TPRS, and the exposure times were increased until the value of  $\theta_D/\theta_L$  reached a steady state. This was then repeated using different gas phase  $P_D/P_L$  ratios.

XPS and TPRS of D-Pro/Cu(111) were performed using a ThermoFisher ThetaProbe consisting of a preparation chamber and an analysis chamber. The preparation chamber houses a sample mount with a heater and temperature controller, a Hiden quadrupole mass spectrometer, an RBD Technologies 04-165 ion gun for sputtering, an evaporative doser for Pro deposition, and a linear translator equipped with a valve to transfer samples between the two chambers. The analysis chamber has an X-ray source, a hemispherical electron energy analyzer, and an ion gun. For XPS, a 400- $\mu$ m spot was exposed to Al K<sub> $\alpha$ </sub> X-rays, and an analyzer pass energy of 40 eV was used to record the kinetic energy of the photo-emitted electrons. Before adsorbing Pro onto Cu(111), the surface was sputtered in the preparation chamber using the Ar<sup>+</sup> ion gun. Then, XPS was performed in the analysis chamber to confirm the cleanliness of the surface by verifying that the carbon, oxygen, and nitrogen coverages were below the detectable limit. After verifying the cleanliness of the Cu(111) surface, the crystal was transferred back to the preparation chamber for adsorption of Pro.

#### 3 | RESULTS

# 3.1 | XPS OF D-Pro/Cu(111)

The chemical states of the Pro multilayer and monolayer on Cu(111) were probed by XPS. While the orientation of the Cu(111) surface differs from those of the Cu(110) and Cu(643)<sup>*R&S*</sup> surfaces used for the TPRS and equilibrium adsorption experiments, prior XPS studies of amino acids on Cu (*hkl*) surfaces have revealed little surface structure dependence to the species observed. Aspartic acid adsorption on Cu(100), Cu(110), and Cu(111) revealed that on all three surfaces, Asp was adsorbed as a zwitterion ( $^{-}O_2$ CCH(NH<sub>3</sub><sup>+</sup>)CH<sub>2</sub>CO<sub>2</sub>H) in the multilayer but as a doubly deprotonated anion ( $^{-}O_2$ CCH(NH<sub>2</sub>)CH<sub>2</sub>CO<sub>2</sub><sup>-</sup>) in the monolayer.<sup>29,42</sup> Furthermore, Cu(111) is relevant as it is the structure of the terrace on the chiral Cu(643)<sup>*R&S*</sup> surfaces. The Pro multilayer was formed by sublimating Pro for 40 minutes onto the Cu(111) surface, with the surface held at 300 K. The same exposure was used to prepare the monolayer, except that the surface was held at 400 K preventing formation of the multilayer. Figure 2 shows the C1*s*, N1*s*, and O1*s* XP spectra of Pro multilayer and monolayer (top and bottom panels, respectively). The solid squares are data points, and the dashed lines are fits using a Shirley background subtraction and a Gaussian-Lorentzian curve fit.

The N1s spectra (Figure 2, center panel) reveal a peak at 402.0 eV (blue dashed curve) in the multilayer that is assigned to the  $>NH_2^+$  group<sup>29</sup> and is absent in the monolayer spectrum. Conversely, there is a peak at 399.5 eV in the monolayer spectrum (red curve) assigned to the >NH group<sup>29</sup> that is present but much less intense in the multilayer spectrum. This indicates that in the D-Pro multilayer, the imine group is protonated while in the monolayer, it is not.

The right panels of Figure 2 show the O1s spectra of multilayer (top) and monolayer (bottom) D-Pro adsorbed on Cu(111). The primary peaks (green curve) reveal a binding energy of approximately 532.0 eV for the multilayer and 531.8 eV for the monolayer. This corresponds to the binding energy of the oxygen atoms in a deprotonated carboxylate species.<sup>29</sup> Since only one major peak is observed for both multilayer and monolayer, it can be concluded that both the oxygen atoms are in similar environments. In other words, the D-Pro carboxylate group is deprotonated in both the monolayer and the multilayer. In contrast, for the Asp/Cu(110) multilayer, the C4 carboxylate remains protonated  $(^{-}O_2CCH(NH_3^+)$ CH<sub>2</sub>CO<sub>2</sub>H) and the O1s spectrum of the Asp multilaver is much broader than the O1s multilayer spectrum of D-Pro/Cu(111).<sup>29</sup> The O1s binding energy of 532.0 eV for the D-Pro/Cu(111) monolayer is consistent with prior observations of Pro O1s spectra at 532.3 eV on TiO2. 43,44

The C1s XP spectra for the D-Pro/Cu(111) multilayer and monolayer are shown in top and bottom left panels of Figure 2, respectively. The C1s spectra for D-Pro/Cu(111) are complex due to the presence of four carbon atoms in the heterocyclic ring and the C1 atom in the carboxylate group. The four carbon atoms in the ring each have different environments, although the two CH<sub>2</sub> groups are likely to have quite similar C1s binding energies. In the multilayer C1s spectrum, a small high binding energy peak is seen at 288.8 eV (red curve), which is assigned to the C1 atom in the deprotonated COO<sup>-</sup> group.<sup>43,45,46</sup> This peak shifts to 287.9 eV in the C1s spectrum of the D-Pro monolayer, as also observed in the case of Ala/Cu(110).<sup>45</sup> The major C1s peaks at 286.3 and 285.1 eV (blue curves) in the multilayer and monolayer XP spectra, respectively, are attributed to the four carbon atoms in the heterocycle



**FIGURE 2** N1*s*, O1*s*, and C1*s* XP spectra of a multilayer (top row panels) and a monolayer (bottom row panels) of D-Pro on Cu(111). The black points are raw data, while the dashed curves are fits used to determine the binding energies. In the multilayer, D-Pro is found to be present in zwitterionic form, indicated by the N1*s* binding energy of 402.1 eV ( $>NH_2^+$ ) and the O1*s* binding energy of 532.1 eV (COO<sup>-</sup>). In the monolayer, the N1*s* peak has shifted to 399.5 eV (>NH) and the O1*s* peak remains at 532.1 eV (COO<sup>-</sup>), suggesting that the D-Pro monolayer is adsorbed in the deprotonated, anionic form on Cu(111)

ring. Although two of the heterocycle carbons are bonded to the *N*-atom, they are not resolvable from the  $CH_2$  groups. The ratio of the C1*s* areas under the ring peak and the COO<sup>-</sup> peak is approximately 3.8, revealing the expected stoichiometry of four ring carbon atoms to one carboxylate carbon atom in the Pro molecule. The shift in binding energy between the multilayer and monolayer suggests that the heterocyclic ring is interacting with the Cu surface in the Pro monolayer.

The binding energies observed in the XP spectra of the C1s, O1s, and N1s core levels suggest that Pro is adsorbed in zwitterionic form in the multilayer, while in the monolayer, it adsorbs as a deprotonated anion with loss of the hydrogen atom from the carboxylate group. This is consistent with the findings of other research groups using XPS to study Pro on Cu and TiO<sub>2</sub> surfaces<sup>41,43,47</sup> but is in contrast to the zwitterionic form found for the Pro monolayer on Pd(111)<sup>36</sup> and the mixture of zwitterion and anionic forms observed on Au(111).<sup>39</sup> Other amino acids including Asp, alanine and glycine on Cu(110) have also been determined to adsorb as anions in the monolayer and zwitterions in multilayer.<sup>29,48,49</sup>

# 4 | Pro DECOMPOSITION ON Cu(111) AND Cu(643)<sup>R</sup>

#### 4.1 | Pro decomposition mechanism

TPRS of D-Pro and isotopically labelled 1-13C-L-Pro was performed on  $Cu(643)^R$  to gain insight into the Pro decomposition mechanism. The experiment was performed by exposing the  $Cu(643)^R$  surfaces to a constant flux of D- or 1-<sup>13</sup>C-L-Pro, with the crystal held at 400 K and using a doser temperature of 333 to 343 K. The TPRS of Pro at  $\theta \cong 0.5$  ML has been chosen as a basis for initial discussion. The behavior of Pro at coverages other than  $\theta \cong 0.5$  is discussed in a later section. After dosing for a specified time (approximately 10 min) to reach a coverage of  $\theta \approx 0.5$  ML, TPRS was performed by heating the surface at 2 K/s and monitoring the signals at m/z = 2 (H<sub>2</sub>), 44  $(CO_2)$ , and 38, 39, 41, and 67 (pyrrole). These m/z ratios were selected based on TPRS performed by other research groups.<sup>36,38,40,50,51</sup> Figure 3 shows the TPRS signals versus temperature for the m/z ratios monitored during D-Pro decomposition. The peak at 475 K in the m/z = 2 signal is consistent with hydrogen desorption because of the



**FIGURE 3** Temperature-programmed reaction spectroscopy (TPRS) of D-Pro adsorbed on Cu(643)<sup>*R*</sup> at  $\theta$  = 0.5 showing signals at m/z = 2, 38, 39, 41, 44, and 67, which are indicative of dehydrogenation of the pyrrolidine ring followed by decomposition into CO<sub>2</sub> and pyrrole. Heating rate was 2 K/s

dehydrogenation of the pyrrolidine ring. Signals at m/z = 38, 39, 41, and 67, consistent with the pyrrole ring and its ionization fragments, are observed at 510 and 570 K, while signal at m/z = 70 (pyrrolidine ring) is not observed. Signal at m/z = 44 (CO<sub>2</sub>) arises from the loss of the carboxylate group of the adsorbed D-Pro. To verify this, the TPRS experiment was repeated with isotopically labelled 1-<sup>13</sup>C-L-Pro, and the signal was observed at m/z = 45 rather than 44, as shown in Figure 4. Thus, the CO<sub>2</sub> originates only from the carboxylate group and can be used to determine relative coverages of D- and 1-<sup>13</sup>C-L-Pro,  $\theta_D/\theta_L$ , after enantiomer co-adsorption.

#### 4.2 | Pro decomposition sites

In the TPRS of Pro/Cu(643)<sup>*R*</sup> (Figure 3), the m/z = 44 peak originating from cleavage of the C1–C<sub> $\alpha$ </sub> bond appears to consist of two separate peaks at  $T_p \cong 535$  K and  $T_p \cong 570$  K. To identify the origin of these two peaks, TPRS of D-Pro was performed on Cu(643)<sup>*R*</sup> at different coverages while monitoring the signals at m/z = 44 and 67 (Figure 5). At  $\theta$ = 0.2 and 0.3, only the peak at approximately 570 K is observed. For  $\theta > 0.5$ , the peak at 535 K appears and grows as the coverage increases. Since the adsorption energy of Pro is likely to be higher on the step edges than on the terrace,<sup>27</sup> one would expect the step edges to be populated at low total Pro coverages and the terraces to be populated once the step edges are saturated with Pro. Within that framework, the observations in Figure 5 suggest that on a high Miller index Cu surface

such as  $Cu(643)^R$ , the step and terrace adsorption sites yield different decomposition kinetics.

To verify the independent site origins of the two CO<sub>2</sub> desorption peaks observed on  $Cu(643)^R$ , TPRS of D-Pro was performed on Cu(111). The peaks for  $CO_2$  and pyrrole desorption on Cu(111) are shown in purple dashed lines in Figure 5. For both CO<sub>2</sub> and pyrrole, a single peak is observed at  $T_p \cong 535$  K the same as that of the lower temperature  $CO_2$  peak on  $Cu(643)^R$ . This suggests that the peak of approximately 535 K in Figure 5 is due to decomposition on the (111) terraces of  $Cu(643)^R$ , while the peak at ~570 K originates from decomposition on the kinked steps of  $Cu(643)^R$ . The experiments on Cu(111) were performed using a different mass spectrometer than the ones on  $Cu(643)^R$ . To compare the TPRS data from the two surfaces, the Cu(111) mass spectrometer signal has been multiplied to match the intensity of mass spectrometer intensity of the  $Cu(643)^R$  data.

# 5 | EQUILIBRIUM ADSORPTION OF Pro ON $Cu(643)^{R\&S}$ AND Cu(110)

## 5.1 | Equilibrium adsorption of D-/L-Pro/ Cu(643)<sup>*R&S*</sup>

To study the enantiospecific aggregation of D-/L-Pro mixtures on Cu(643)<sup>*R&S*</sup>, equilibrium adsorption experiments were performed. Briefly, the clean surface was exposed for a range of times to a flux with constant  $P_D/P_L$  in the gas phase. After each exposure, TPRS was performed to

**FIGURE 4** Temperature-programmed reaction spectroscopy (TPRS) of D- and  $1^{-13}$ C-L-Pro (separate experiments) on Cu(643)<sup>*R*</sup> at  $\theta = 1$ . D-Pro decomposition yields signal at m/z = 44 (solid blue line) but not at m/z = 45 (dashed blue line).  $1^{-13}$ C-L-Pro yields signal at m/z = 45 (solid red line) but not at m/z = 44 (dashed red line). This enables quantification of  $\theta_L/\theta_D$ in mixed monolayers of D-Pro and  $1^{-13}$ C-L-Pro

 $CO_2$ desorption rate (a.u.) FIGURE 5 Temperature-programmed reaction spectroscopy (TPRS) of CO<sub>2</sub> (m/z = 44) and pyrrole (m/z = 67)desorption (solid lines) during D-Pro decomposition on  $Cu(643)^R$  while heating at 2 K/s. Initial D-Pro coverages were  $C_4H_4N$  $\theta_{Pro} = 0.2, 0.3, 0.6, 0.8, and 1.$  Both CO<sub>2</sub> and pyrrole TPRS show two peaks that may be attributable to different decomposition kinetics on the steps and terraces of  $Cu(643)^R$ . TPRS of  $CO_2$  and pyrrole desorption (violet dotted lines) on Cu(111) are also shown. These exhibit 500 450 kinetics consistent with the lowtemperature decomposition peak observed



determine the D-/L-Pro coverage ratio,  $\theta_D/\theta_L$  on the surfaces. The exposure times were increased until  $\theta_D/\theta_L$  reached equilibrium with the gas phase. This experiment was then repeated using different  $P_D/P_L$  values to determine the equilibrium values of  $ee_s = \frac{\theta_D - \theta_L}{\theta_D + \theta_L}$  versus  $ee_g = \frac{P_D - P_L}{P_D + P_L}$ . The relationship between  $ee_s$  and  $ee_g$ 

on  $Cu(643)^R$ 

 $P_{\rm D} + P_{\rm L}$  reveals the tendency for homochiral aggregation,

heterochiral aggregation, enantiospecific adsorption, or lack of enantiospecific organization.<sup>28,52,53</sup>

To calibrate the incident flux ratios versus doser temperature,  $P_{\rm D}/P_{\rm L}$ , TPRS was performed after short exposure times to determine whether  $\theta_{\rm D}/\theta_{\rm L}$  is constant at sub-monolayer coverages,  $\theta = \theta_{\rm D} + \theta_{\rm L} < 1$ . The assumption in this procedure is that at low total coverages, the sticking coefficients of D- and L-Pro are equal (and probably close to unity) on the clean Cu(643)<sup>*R*</sup> surface. It also

assumes that at low coverages, the two enantiomers are not displacing one another and that displacement kinetics only become significant when  $\theta \approx 1$ . These assumptions being the case, the value of  $\theta_D/\theta_L$  at submonolayer coverage can be assumed to be a measure of  $P_D/P_L$ . These assumptions have held during prior work with Asp, serine, alanine, and phenylalanine on Cu surfaces,<sup>54-56</sup> but they seem to fail in the case of Pro. TPRS experiments were performed by exposing Cu(643)<sup>*R*</sup> at 400 K to a gas



**FIGURE 6** Variation of  $\theta_D/\theta_L$  with total Pro coverage,  $\theta$ , on Cu(643)<sup>*R*</sup> held at 400 K when the surface is exposed to fluxes of Dand L-Pro simultaneously.  $\theta_D/\theta_L$  changes significantly even at submonolayer coverages, making the determination of  $P_D/P_L$ challenging



phase mixture of D-/L-Pro for exposure times in the range 0 to 45 minutes. Figure 6 plots  $\theta_D/\theta_L$  versus total Pro coverage,  $\theta$ , with measurements made nonsequentially with respect to exposure time and total coverages of  $\theta < 1$ . The values of  $\theta_D/\theta_L$  vary significantly from the extrapolated *y*-intercept of  $\theta_D/\theta_L = 1.5$  that might be assumed to be a good estimate of  $P_D/P_L$ . These data suggest that Pro enantiomers displace one another enantiospecifically, even at coverages of  $\theta \ll 1$ , something not observed with other amino acids.

To measure a reproducible and credible value of  $P_{\rm D}/P_{\rm L}$ , TPRS experiments were performed with the surface held at 200 K so that a multilayer forms and one can measure the ratio of enantiomers in the multilayer. In the multilayer, the ratio of D-/L-Pro should equal to  $P_{\rm D}/P_{\rm L}$  since no surface adsorption/aggregation effects are at play and the sticking coefficient is likely to be close to unity at the 200 K adsorption temperature. Figure 7 shows TPRS results obtained following multilayer adsorption of an approximately 2.1:1 D-/L-Pro gas phase mixture on  $Cu(643)^R$  at 200 K. The monolayer decomposition peaks at m/z = 44 and 45 occur over the temperature range 480 to 600 K. At approximately 320 K, m/z = 44and 45 peaks are seen that exhibit the zero-order kinetics typical of multilayer desorption. The areas under the m/z. = 44 and 45 peaks of the multilayer can be used to quantify  $P_{\rm D}/P_{\rm L}$ . To verify that the multilayer peaks can be used to quantify  $P_{\rm D}/P_{\rm L}$ , multilayer experiments were repeated with the same D-/L-Pro gas phase mixture of approximately 2.1:1 for four different exposure times of 20, 40, 60, and 80 minutes. For all four exposure times, the area

**FIGURE 7** Temperature-Programmed Reaction Spectroscopy (TPRS) obtained after exposure of Cu(643)<sup>*R*</sup> at 200 K to a flux of approximately 2.1:1 D-/L-Pro for 30 minutes. The peaks at m/z = 44 and m/z = 45 at 480 to 600 K arise from decomposition of the Pro monolayer. The additional peaks at approximately 320 K arise from multilayer desorption. It is clear that the ratio of enantiomers in the multilayer differs from that in the monolayer

ratios under the multilayer peaks at m/z = 44 and 45 remained constant in the range 2 to 2.3, suggesting that the ratio of m/z = 44 and 45 in the multilayer TPRS peaks represents the gas phase composition.

One of the primary goals of this work is to determine the relationship between the enantiomeric excess in the equilibrium coverages,  $ee_s = \frac{\theta_D - \theta_L}{\theta_D + \theta_L}$ , on the Cu(643)<sup>*R&S*</sup> surfaces and the enantiomeric excess of D-/L-Pro mixtures in the gas phase,  $ee_g = \frac{P_D - P_L}{P_D + P_L}$ . Figure 8 shows the results of the equilibrium adsorption experiments using D-/L-Pro mixtures on both Cu(643)<sup>*R&S*</sup> surfaces. This plots the evolution of  $\theta_D/\theta_L$  versus exposure time to D-/L-Pro mixtures with various values of  $P_{\rm D}/P_{\rm L}$ . Typically, for each set of experiments using a different value of  $P_{\rm D}/P_{\rm L}$ , two or three different multilayer adsorption experiments using 30 to 50 minutes exposure times and a surface temperature of 200 K were performed to determine  $P_{\rm D}/P_{\rm L}$ . In these experiments, the Pro doser temperatures were maintained such that the total gas phase flux was in the range 0.1 to 0.2 monolayers/min. Figure 8 shows that on exposing  $Cu(643)^{R}$  and  $Cu(643)^{S}$  (empty and filled black squares, respectively) to a racemic mixture with  $P_{\rm D}/P_{\rm L} = 1$ , the monolayer remains racemic, ie,  $\theta_{\rm D}/\theta_{\rm L} \cong 1$ . This demonstrates that Pro adsorption is not enantiospecific, in spite of the fact that the Cu(643)<sup>R&S</sup> surfaces are chiral. However, on exposing the surfaces to fluxes with  $P_{\rm D}/P_{\rm L} > 1$ , the resulting equilibrium values of  $\theta_D/\theta_L$  are amplified relative to  $P_{\rm D}/P_{\rm L}$ , with both surfaces becoming enriched in D-Pro, the majority gas phase enantiomer. For example,  $P_{\rm D}/P_{\rm L} = 1.9$  yields  $\theta_{\rm D}/\theta_{\rm L} = 4$ , and  $P_{\rm D}/P_{\rm L} = 3.1$  yields  $\theta_{\rm D}/\theta_{\rm L}$ = 12. Similarly, when the surfaces are exposed to fluxes

with  $P_{\rm D}/P_{\rm L} < 1$ , they becomes enriched in L-Pro and  $\theta_{\rm D}/\theta_{\rm L} < P_{\rm D}/P_{\rm L}$ , independent of surface chirality. In other words, independent of surface chirality, the Cu(643)<sup>*R&S*</sup> surfaces become enriched in the Pro enantiomer that is in excess in the gas phase.

In order to demonstrate that the long-time, steadystate values of  $\theta_{\rm D}/\theta_{\rm L}$  being measured in Figure 8 are equilibrium values, adsorption experiments (Figure 9) were performed wherein the surface was exposed to a constant gas phase flux,  $(P_{\rm D}/P_{\rm L})_1$ , for 15 minutes to generate a coverage ratio  $(\theta_{\rm D}/\theta_{\rm I})_1$ , and then to a second flux,  $(P_{\rm D}/P_{\rm I})_2$ for increasing times. The value of  $(P_{\rm D}/P_{\rm L})_2$  was chosen such that its corresponding equilibrium coverage ratio,  $(\theta_{\rm D}/\theta_{\rm L})_2$ , is less than the coverage ratio,  $(\theta_{\rm D}/\theta_{\rm L})_1$ , generated by the initial exposure to  $(P_{\rm D}/P_{\rm L})_1$ . The data in Figure 9 demonstrate that the steady-state coverage ratios are independent of whether one exposes only to  $(P_{\rm D}/P_{\rm L})_2$ or to the sequence  $(P_{\rm D}/P_{\rm L})_1$  followed by  $(P_{\rm D}/P_{\rm L})_2$ . In other words, when using  $(P_{\rm D}/P_{\rm L})_2$ , the same steady-state value of  $(\theta_{\rm D}/\theta_{\rm L})_2$  is reached independent of whether the initial coverage ratio is either greater or less than  $(\theta_D/\theta_L)_2$ . This suffices to demonstrate that the steady-state value of  $\theta_{\rm D}/\theta_{\rm L}$  is a good measure of the equilibrium coverage ratio.

### 5.2 | Equilibrium adsorption of D-/L-Pro/ Cu(110)

As discussed earlier, STM observations of Pro/Cu(110) have revealed the formation of a pseudo-racemate structure that is interesting, given that such pseudo-racemate structures (random solid solutions of enantiomers) are rarely observed in three dimensions.<sup>23,57</sup> To probe the







**FIGURE 9** Evolution versus exposure time of  $\theta_D/\theta_L$  for D-/L-Pro on the Cu(643)<sup>*R*</sup> surface held at 400 K when starting with  $(P_D/P_L)_1 = 2.1$  (or 0.6) and then changing the gas phase ratio to  $(P_D/P_L)_2 = 1.3$ (or 0.75) after a monolayer is reached at 15 minutes (dashed curves). These are compared with data taken starting with  $(P_D/P_L)_2 = 1.3$  (or 0.75) (solid curves). The fact that in both experiments, the steadystate ratio is independent of exposure protocol indicates that the steady-state coverages are a measure of equilibrium between  $\theta_D/\theta_L$  and  $P_D/P_L$ 

characteristics of this state, we have performed equilibrium adsorption experiments for D-/L-Pro/Cu(110), similarly to those just discussed for the Cu(643)<sup>*R&S*</sup> surfaces. Adsorption experiments on Cu(110) were performed with D-Pro and isotopically labelled <sup>15</sup>N,1-<sup>13</sup>C-L-Pro to allow multilayer experiments to aid in measuring  $P_D/P_L$ . Because the nitrogen atom of L-Pro is labelled with <sup>15</sup>N, mass spectra of D-/L-Pro mixtures contain signals at both m/z = 70 and 71, corresponding to D-Pro and <sup>15</sup>N,1-<sup>13</sup>C-L-Pro, respectively. During multilayer desorption, the signals at m/z = 70 and 71 were monitored to estimate the value of  $P_D/P_L$ .

Equilibrium adsorption experiments using D-/L-Pro on Cu(110) were performed with the surface at 450 K and at a total D-/L-Pro flux of approximately 0.2 ML/min. These were experimentally verified to be the conditions under which displacement of enantiomers occurs on the Cu(110) surface. A saturated monolayer of one Pro enantiomer on Cu(110) was exposed to a flux of the opposite enantiomer for various periods of time, after which TPRS was used to demonstrate that some fraction of the initially adsorbed enantiomer had been displaced by the opposite enantiomer in the gas phase.

The experimental procedure for equilibrium adsorption of D-/L-Pro mixtures on Cu(110) at 450 K was the same as that described for measurements on Cu(643)<sup>*R&S*</sup> at 400 K in the previous section. Figure 10 plots the evolution of  $\theta_D/\theta_L$  on Cu(110) as a function of exposure time for different values of  $P_D/P_L$ . The data fit with solid curves were obtained by starting with a clean Cu(110) surface. Even at long exposure times,  $\theta_D/\theta_L$  remains constant and equal to  $P_{\rm D}/P_{\rm L}$ . To verify that  $\theta_{\rm D}/\theta_{\rm L}$  measured on the Cu(110) surface is a good estimate of the equilibrium value, an experiment was performed wherein the Cu(110) surface was first saturated with  $\theta_{\rm D}/\theta_{\rm L} = 0.5$  and then exposed to  $P_{\rm D}/P_{\rm L} = 1.9$ . The data fit with the dashed curve and open symbols plot the evolution of  $\theta_{\rm D}/\theta_{\rm L}$  when starting with  $(\theta_{\rm D}/\theta_{\rm L})_0=0.5$  and then exposing to a D-/L-Pro mixture with  $P_{\rm D}/P_{\rm L} = 1.9$ . Under these conditions, the Pro coverage ratio approaches  $\theta_{\rm D}/\theta_{\rm L} = P_{\rm D}/P_{\rm L}= 1.9$ . This last experiment was performed at the same total gas phase flux of approximately 0.2 ML/min and surface temperature of 450 K as the other experiments in Figure 10.

The data for these equilibrium adsorption measurements on Cu(643)<sup>R&S</sup> and Cu(110) are best represented by plotting  $ee_s$  versus  $ee_g$  as shown in Figure 11. In summary, the equilibrium enantiomer adsorption isotherm in Figure 11 shows that the D-/L-Pro enantiomer ratio on the Cu(110) surface remains the same as the enantiomer ratio in the gas phase; i.e.,  $ee_s = ee_g$ . This implies that there is no net driving force for either homochiral or heterochiral aggregation of D-/L-Pro mixtures on Cu(110). If indeed there was a propensity for homochiral aggregation to occur on Cu(110), the adsorption isotherm for Pro/Cu(110) would look very similar to the one for  $Pro/Cu(643)^{R\&S}$ . If homochiral aggregation was preferred, then the presence of a majority enantiomer in the gas phase would lead to displacement of the opposite enantiomer from the surface, yielding a value of  $|ee_s| > |ee_{g}|$ . Our observation is consistent with the STM observation of a pseudo-racemate on Cu(110).<sup>23,57</sup> In contrast, the



**FIGURE 10** Evolution of  $\theta_D/\theta_L$  versus exposure time for D-/L-Pro on the Cu(110) surface held at 450 K and using different values of  $P_D/P_L$ . The data plotted with solid symbols and solid lines were obtained by starting with an initially clean surface. The data plotted with open symbols and a dashed line were obtained by starting with the surface covered with  $\theta_D/\theta_L = 0.5$  and then exposing to  $P_D/P_L = 1.9$ 



**FIGURE 11** Adsorption isotherm of D-/L-Pro on Cu(643)<sup>*R&S*</sup> and Cu(110) obtained by plotting the equilibrium values of *ee<sub>s</sub>* versus  $ee_g$ . The data for Pro reveal that  $|ee_s| > |ee_g|$  on Cu(643)<sup>*R&S*</sup>, while on Cu(110), the surface enantiomer ratio remains the same as the gas phase enantiomer ratio,  $ee_s = ee_g$ 

same experiments performed on the Cu(643)<sup>*R&S*</sup> surfaces clearly reveal that Pro does not exhibit enantiospecific adsorption;  $ee_s(ee_g = 0) = 0$ . The data do reveal a propensity for homochiral aggregation of Pro mixtures on Cu(643)<sup>*R&S*</sup> surfaces resulting in amplification of the enantiomeric excess on the surface with respect to the enantiomeric excess in the gas phase;  $|ee_s| > |ee_g|$ .

# 5.3 | ADSORPTION ISOTHERM OF Pro ON Cu(643)<sup>*R&S*</sup> AND Cu(110)

The enantiospecific adsorption isotherm (Figure 11) of  $ee_s$ versus  $ee_{\alpha}$  for mixtures of D-/L-Pro on Cu(643)<sup>*R&S*</sup> is similar to one published for Asp/Cu(643)<sup>R&S 28</sup> Figure 11 shows that when one enantiomer is in the majority in the gas phase  $(ee_g \neq 0)$ , the Cu(643)<sup>*R&S*</sup> surfaces are enriched in that enantiomer at equilibrium. In the case of a racemic gas phase mixture with  $ee_g = 0$ , the adsorbed monolayer remains racemic,  $ee_s(ee_g = 0) = 0$ , indicating that there are no enantiospecific interactions of the adsorbed D- and L-Pro with the chiral  $Cu(643)^{R\&S}$  surfaces. For non-racemic mixtures, enrichment of the surface in the majority gas phase enantiomer implies that attractive homochiral interactions (D-D and L-L) are stronger than the heterochiral interactions (D-L).<sup>52</sup> Thus, Pro on Cu(643)<sup>*R&S*</sup> exhibits homochiral aggregation. This behavior is similar to that observed for  $Asp/Cu(643)^{R\&S}$ in terms of homochiral amplification but to a much stronger degree for Pro than for Asp. In the case of D-/L-Pro on Cu(110),  $ee_s = ee_g$  throughout the range  $ee_g = +1$  to -1. Thus, Pro/Cu(110) displays neither enantiospecificity nor aggregation.

A Langmuir adsorption model has been developed to account for the role of enantiospecific clustering on surfaces.<sup>28,52,53</sup> Conventionally, the Langmuir model of adsorption assumes no adsorbate-adsorbate interactions. However, the model can be modified to account for aggregation by introduction of an equilibrium constant,  $K_c$ , for aggregation of adsorbed monomers into

homochiral or heterochiral clusters and introduction of an additional parameter, namely, cluster size, *n*. The adsorption isotherm in Figure 11 has been fit to this modified Langmuir model using two parameters, cluster size and equilibrium constant of homochiral aggregation,  $K_c$ . The dashed magenta line in Figure 11 shows the fit to the adsorption isotherm. The free energy of homochiral aggregation can be estimated using  $G = RT \cdot ln(K_c)$ . The best fit values of  $\Delta G$  and *n* were found to be 3.3 kJ/mol and 14, respectively. In contrast, the values of *G* for homochiral aggregation of Asp on Cu(643)<sup>*R&S*</sup> is 2.2 kJ/mol.<sup>28</sup>

### 5.4 | ADSORPTION ISOTHERM OF PSUEDO-RACEMATE STATE FOR D-/L-Pro ON Cu(110)

It is pertinent to discuss our findings for equilibrium adsorption of D-/L-Pro on Cu(110) in the context of the STM results of Raval et al. for the structure of DL-Pro/ Cu(110).<sup>23</sup> The distinction in our notation for mixtures of Pro enantiomer is that DL-Pro implies a racemic mixture, whereas D-/L-Pro can be of any composition. Their STM experiments were performed at 300 K and determined that the ordered  $(4 \times 2)$  overlayer that is formed by DL-Pro/Cu(110) is a random solid solution of enantiomers, i.e., a pseudo-racemate. This is consistent with there being no strong intermolecular forces that would lead to formation of either racemate or conglomerate domains. When a non-racemic mixture of enantiomers adsorbs on a surface during the equilibrium adsorption experiment,  $\theta_{\rm D}/\theta_{\rm L} = P_{\rm D}/P_{\rm L}$  implies that there is no enantiospecific aggregation or enantiospecific adsorption. Because Cu(110) is achiral, adsorption on the surface cannot be enantiospecific, so  $ee_s(ee_s = 0) = 0$ . The fact that  $ee_s = ee_g$  at all values of  $ee_g$  indicates a lack of enantiospecific adsorbate-adsorbate interactions leading to either homochiral or heterochiral aggregation. Thus, the equilibrium adsorption experiments are consistent with the STM observations of DL-Pro/Cu(110) made by Raval et al. This is the first time that findings of our equilibrium adsorption experiment have been compared with a system that has been probed using STM.

### 6 | CONCLUSION

The decomposition and equilibrium adsorption of D-/L-Pro on  $Cu(643)^{R\&S}$  and Cu(110) and Cu(111) have been studied. Pro was found to adsorb as an anion on the Cu(111) surface. Using isotopic labelling, it was found that the decomposition of Pro on  $Cu(643)^{R\&S}$  led to the cleavage of the C1-C2 bond, yielding  $CO_2$  in the gas phase and

pyrrole on the suface. On the Cu(643)<sup>*R&S*</sup> surface, Pro decomposition exhibits different kinetics on the kinked steps vs the terraces. Pro was found to exhibit homochiral aggregation on Cu(643)<sup>*R&S*</sup> while exhibiting no preference for either homochiral or heterochiral aggregation on Cu(110). The latter is an interesting observation in the light of previous STM studies of D-/L-Pro on Cu(110) that found Pro enantiomers forming a random solid solution phase on Cu(110). This is the first adsorbate-surface system that has been studied using both STM and equilibrium adsorption experiments and reveals a convergence between STM observations and equilibrium adsorption experiments.

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