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[abstract]

ABSTRACT

The chemisorption and electrochemical activity of 2,5-dihydroxythiophenol (DHT) and 2-(8-mercaptooctyl)-1,4-benzenediol (DHOT) on well-defined Pd(111) surfaces were studied by Auger electron spectroscopy (AES), low energy electron diffraction (LEED), high resolution electron energy-loss spectroscopy (HREELS), and electrochemistry (EC). Results confirm that DHT is chemisorbed in two discrete orientations such that at low concentrations, DHT is oxidatively bound to the surface through the diphenol and mercapto groups as quinonoid and S moieties, respectively, whereas at high concentrations, the molecule is coordinated oxidatively through the –SH group in a vertical S- η^1 orientation. When DHT is chemisorbed in a vertical orientation, the diphenol group is pendant and thus exhibits reversible quinone/diphenol redox activity. However, when the compound acts as a bidentate ligand (at low concentrations), the ring loses its redox activity. Iodine was then found to displace the coordinated quinone ring causing it to regain its electrochemical activity. Electrochemical results also show that by comparing the redox behavior of chemisorbed DHT and DHOT, interactions between DHT molecules on the Pd(111) surface are indeed found to be mediated by the surface.

[abstract]

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INTRODUCTION

In heterogeneous catalysis, it is important to fundamentally understand the various interactions that occur at the surface. These interactions include those between adsorbed molecules on the substrate, between the substrate and the chemisorbed molecules¹ as well as those between adsorbates that are mediated by the substrate.²⁻⁵ In electrocatalysis and for redox centers immobilized onto electrode surfaces indirectly by an anchor group, substrate-mediated interactions may occur between pendant electroactive groups if they are surface-active and are not positioned too distant from the metal surface.⁵

Substrate-mediated interactions can be perceived in terms of mixed-valence metal complexes. The main difference is that the metal centers interact through a ligand, which contains delocalized

electrons, in mixed-valence complexes while in substrate-mediated adsorbate-adsorbate interactions, the electroactive species interact through the electrons at the metal surface. It is also important to point out that on the latter, surface activities of the adsorbed molecules also depend on the chemisorption orientation.⁵

In an earlier work, it was proposed that when 2,5-dihydroxythiophenol (DHT) is chemisorbed through the -SH group in a vertical S- η^1 orientation on the Pd(111) surface, adsorbate-adsorbate interactions are mediated by the surface.⁵ If these intermolecular interactions indeed occur through the substrate, then a non-conductive spacer should block the communication between adjacent molecules. It is in this regard that the current study is undertaken. This investigation compares the behavior of DHT and 2-(8-mercaptooctyl)-1,4-benzenediol (DHOT) chemisorbed on a well-defined Pd(111) single crystal surface. The structural difference between these two molecules is merely the presence of a non-conductive alkyl chain between the -SH group and the diphenolic ring in DHOT.

It was also proposed that using high aqueous solution concentrations, DHT is oxidatively chemisorbed through the -SH group in a vertical orientation such that the pendant diphenol group exhibits reversible quinone/diphenol redox activity whereas at low concentrations, the diphenol and mercapto groups are oxidatively coordinated to the surface as quinonoid and S moieties, respectively, causing the molecule to lose its redox activity. In order to ascertain these discrete orientations or this orientational transition, this research was also carried out.

EXPERIMENTAL

Electron spectroscopy measurements were performed in an all stainless steel ultrahigh vacuum (UHV) system described elsewhere.⁶ The Pd(111) single crystal was cleaned by Ar⁺-ion bombardment and oxygen burning and the surface order was regenerated by high-temperature annealing. The smoothness of the Pd(111) surface was confirmed by low energy electron diffraction (LEED, Perkin-Elmer), and the surface composition was verified by both Auger electron spectroscopy (AES, Perkin Elmer) and high resolution electron energy-loss spectroscopy (HREELS, LK 2000, LK Tech) prior to all measurements. The analysis procedure is presented elsewhere.^{5,7,8}

All aqueous solutions were prepared utilizing Milli-Q Plus water (Aldrich). All solutions used in the surface analysis experiments contained 1 mM sulfuric acid (Aldrich) as the supporting electrolyte.

Potential control during the electrochemical experiments was done using a conventional potentiostat (CV-27, Bioanalytical Systems Inc., West Lafayette, IN). Electrode potentials were referenced to a Ag/AgCl (1 mM NaCl) electrode in a cell compartment separated from the working electrode by a fine glass frit. A Pt wire was used as an auxiliary electrode.

Synthesis of 2,5-Dihydroxythiophenol (DHT)

The synthesis of DHT was based upon published procedure.⁹ Twenty-six grams of benzoquinone (0.2 mol) was dissolved in 75 ml glacial acetic acid and heated to 40-50 °C. Seventy-five grams of sodium thiosulfate was dissolved in 100 mL water. The previously prepared benzoquinone solution was slowly added to the sodium thiosulfate solution. The resulting mixture was stirred for 2 minutes. Potassium chloride (KCl) was then added to this mixture until copious amounts of white precipitate (2,5-dihydroxyphenylthiosulfate) appeared. After 2 hours, the precipitate was filtered out and rinsed with concentrated KCl solution. The precipitate was then left in the dark to dry for 12 hours.

A 2.6-gram sample of 2,5-dihydroxyphenylthiosulfate was dissolved in a mixture of 26 mL water and 20 mL concentrated HCl. Five grams of zinc powder was slowly added to the above solution and the temperature was carefully maintained at 40-50 °C. The product was extracted with ethyl ether at room temperature and the organic phase was poured onto a Petri dish and transferred to a desiccator. Recrystallization in benzene was done to achieve higher purity. Mass spectrometry was used to verify

that the purity of the synthesized DHT was at least 95%.

Synthesis of 2-(8-mercaptooctyl)-1,4-Benzenediol (DHOT)

The synthesis of DHOT was described in a previous report.¹⁰

RESULTS AND DISCUSSION

The red current-potential curve in Figure 1 shows the positive potential segment of the cyclic voltammogram of DHT chemisorbed on a Pd(111) surface from a 0.02-mM solution. It can be observed that there is no discernable anodic current that may be due to the oxidation of the dihydroxy molecule (hydroquinone, H₂Q) to the dicarbonyl species (benzoquinone, Q). Previous studies on polycrystalline electrodes revealed that when DHT is chemisorbed at low coverages on Au, the Q/H₂Q redox behavior is preserved. This indicates that on the Au surface, the molecule is attached through the mercapto group and the diphenolic moiety remains fully pendant making the ring electroactive. However, when DHT was chemisorbed at low coverages on Pt, no redox activity was observed.¹¹ Such loss of activity was rationalized to be due to the oxidative chemisorption of the diphenolic ring in addition to that of the -SH group. Hence, at very low coverages, both the -SH and diphenolic groups simultaneously bind to the Pt surface. Similar results were also obtained for Ir.^{12,13} Based on these results, it is to be expected that an identical adsorption structure would also transpire at the Pd(111) electrode surface.

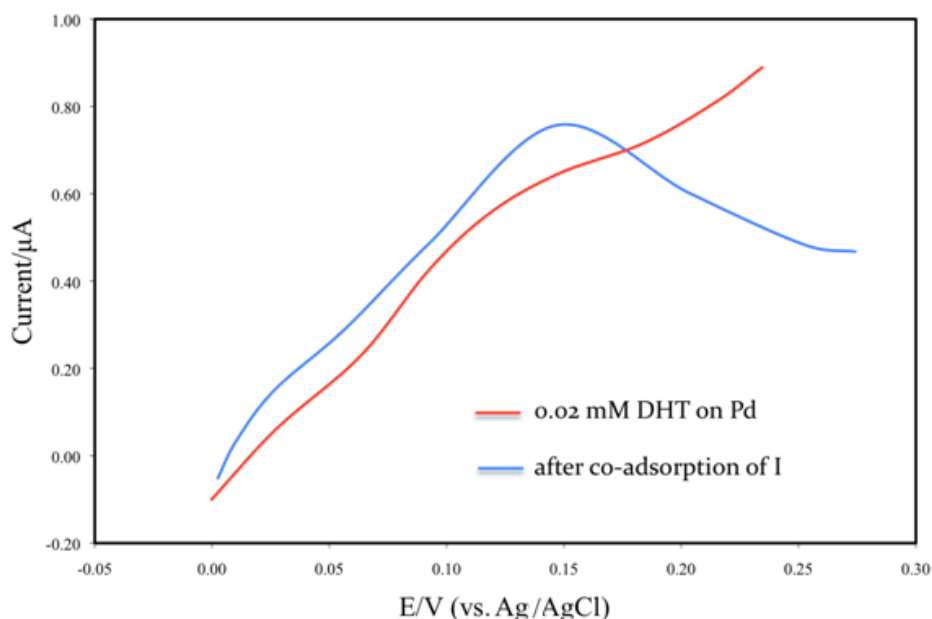


Figure 1. Positive current-potential curves of DHT chemisorbed on a Pd(111) surface prepared from a 0.02-mM solution before (red) and after (blue) co-adsorption of I. Scan rate: 2 mV/sec.

The Pd surface that contained the chelated DHT molecules was exposed to a dilute solution of KI and the resulting voltammogram is shown as a blue curve in Figure 1. It was found earlier that I⁻ is much more surface active than the diphenolic ring.^{3,14,15} Hence, co-adsorption of iodine with the chelated DHT molecule on the surface would result in the displacement of the aromatic ring. The then pendant diphenolic moiety (still attached to the surface through the mercapto group) would then exhibit its

reversible quinone-to-diphenol redox activity. This is indeed what is observed in the blue current-potential curve in Figure 1. The voltammetric features are quite similar to those obtained from similar experiments on polycrystalline Pt.¹¹

When DHT is chemisorbed from a much higher concentration, it is expected to bind exclusively via the mercapto group. In this case, since the diphenolic ring is pendant, reversible quinone-to-diphenolic redox activity would be exhibited. This is definitely apparent on the cyclic voltammogram of DHT chemisorbed from a 5-mM solution as shown in Figure 2. It is also obvious that co-adsorption of I⁻ does not alter the redox activity since the molecule is currently in a vertical orientation.

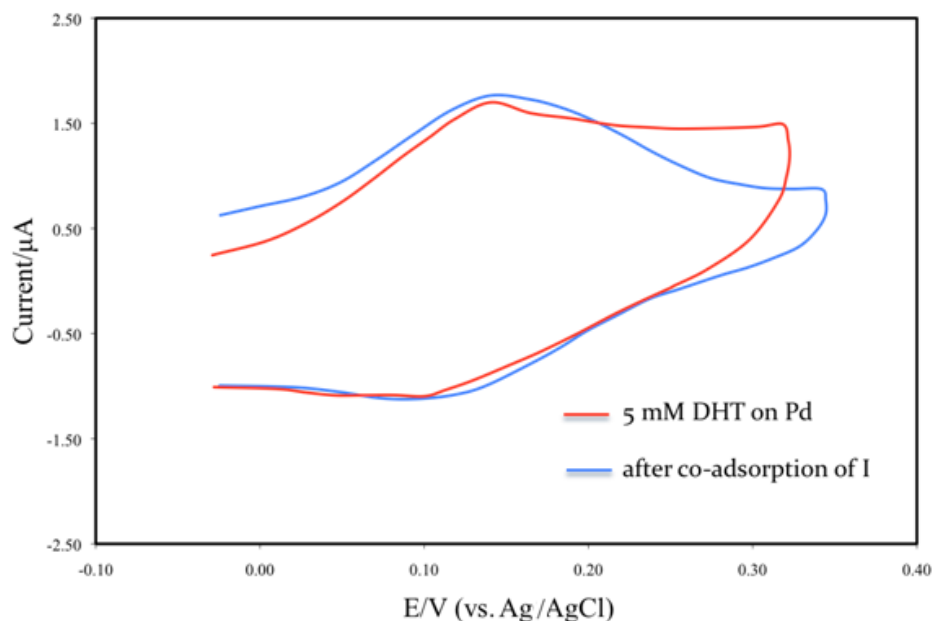


Figure 2. Cyclic voltammograms of chemisorbed DHT on a Pd(111) surface prepared from a 5-mM solution before (red) and after (blue) co-adsorption of I. Scan rate: 2 mV/sec.

It is important to recall earlier voltammetric experiments of DHT chemisorbed on Au and Pt. It was found that the redox peaks are abnormally broad for DHT on Pt but not on Au.^{3,11,13} It was further found out that: (a) peak broadening is induced by attractive interactions between adsorbed molecules;^{16,17} (b) such attractive forces are similar to those in the quinhydrone (1:1 Q:H₂Q) complex and favor the formation of a 1:1 Q-to-H₂Q ratio within the chemisorbed DHT layer;¹⁸ (c) the full width at half maximum (FWHM) of DHT on Pt (0.21 V) is much larger than that on Au (0.13 V) due to a stronger affinity of the diphenolic moiety to the Pt surface relative to the Au surface; (d) when a -CH₂- group, which does not possess delocalized electrons, is inserted between the diphenolic ring and the -SH group, as in the case of 2,5-dihydroxy-4-methylbenzenemercaptan (DHBM), the peak broadening effect disappeared on Pt.^{2,11,13,19,20} Based on these results, it was postulated that the adsorbate-adsorbate interaction that led to the redox peak broadening occurred through the substrate and not through space; no such substrate-mediated interaction occurred on Au because the aromatic ring is inert towards it.

As an extension to the DHT studies, DHOT was also investigated. As mentioned above, insertion of a non- π -system like -CH₂- between the -SH and the diphenolic group disrupted the substrate-mediated adsorbate-adsorbate interactions on Pt. Hence, the presence of an 8-carbon alkyl chain on DHOT should disrupt the intermolecular interactions that transpire at the Pd surface. That is, no voltammetric

peak broadening should be observed. Figure 3 provides voltammetric data that corroborates this idea; the voltammetric FWHM of chemisorbed DHOT, which is 0.13 V, is significantly smaller than that of DHT, which is 0.19 V. In addition, the redox behavior of the diphenolic moiety remains unchanged after the co-adsorption of I.

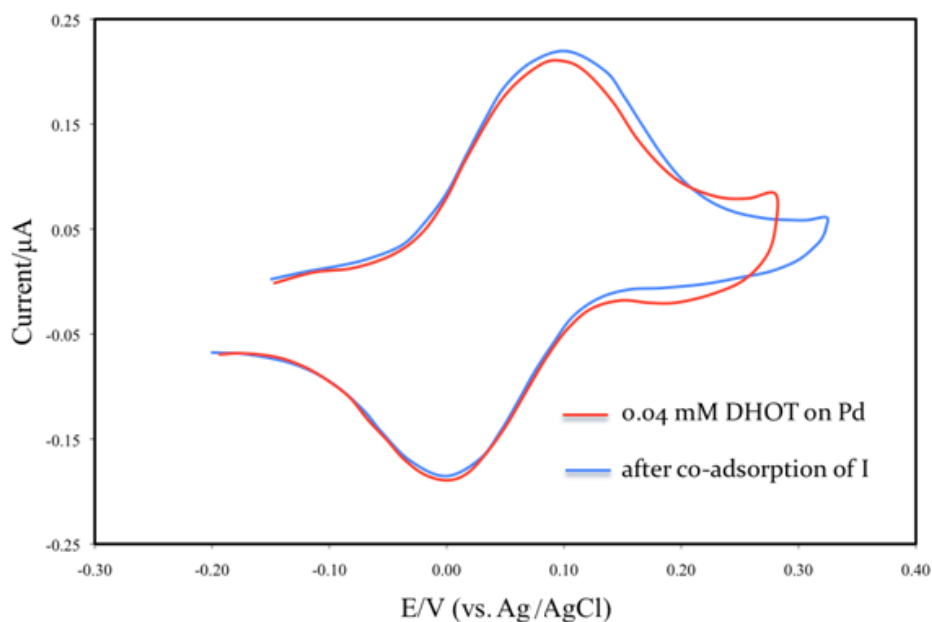


Figure 3. Cyclic voltammograms of chemisorbed DHOT on a Pd(111) surface prepared from a 0.04-mM solution before (red) and after (blue) co-adsorption of I. Scan rate: 2 mV/sec.

HREELS experiments on chemisorbed DHT on Pd(111) were also carried out. Figures 4 and 5 show the HREEL spectra of the Pd surface emersed from 0.02-mM and 5-mM solutions of DHT, respectively; peak assignments are listed in Table 1.^{21,22} Pd- η^7 -S-Q represents DHT chemisorbed as a bidentate ligand on the Pd surface as obtained after immersing the Pd electrode to the 0.02-mM DHT solution. On the other hand, Pd- η^1 -S-H₂Q denotes DHT chemisorbed through sulfur with the H₂Q group pendant as a result of immersing the electrode to the 5.0-mM solution.

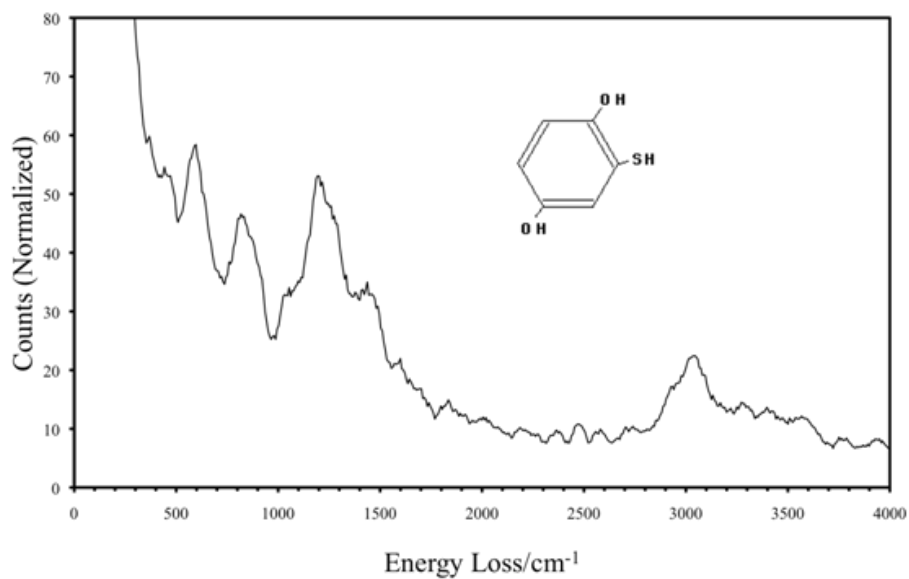


Figure 4. HREEL spectrum of DHT chemisorbed on a Pd(111) surface from a 0.02-mM solution. Experimental conditions: incident beam energy = 3.67 eV; incidence and detection angles = 62° from surface normal; beam current = 55 pA.

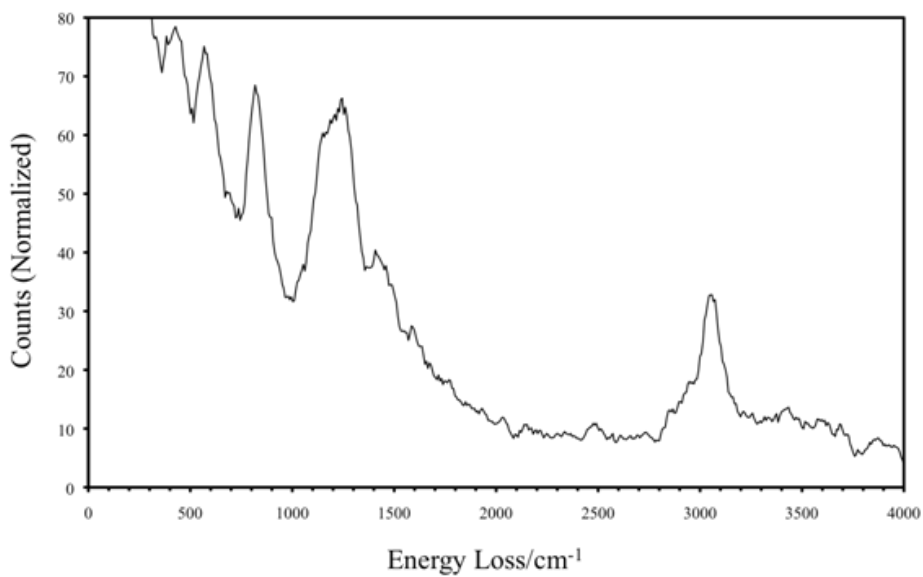


Figure 5. HREEL spectrum of DHT chemisorbed on a Pd(111) surface from a 5-mM solution. Experimental conditions: incident beam energy = 3.67 eV; incidence and detection angles = 62° from surface normal; beam current = 55 pA.

Table 1. HREELS peak assignments for DHT chemisorbed on Pd(111)

| Energy Loss Pd-h7-S-Q (cm ⁻¹) | Energy Loss Pd-h1-S-H2Q (cm ⁻¹) | Energy Loss Pt-h1-S-H2Q ^a (cm ⁻¹) | Vibrational Mode ^b |
|---|---|--|----------------------------------|
| 442 | 420 | 409 | d(CC) |
| 803 | 818 | 821 | g(CH) |
| 1186 | 1149,1238 | 1171 | n(CO), d(CH) |
| 1437 | 1407 | 1463 | d(OH) |
| 1599 | 1584 | 1574 | n(CC) |
| 3036 | 3043 | 3048 | n(CH) |
| noisy | noisy | 3508 | n(OH) |

^aSee Reference²²

^bg^o out-of-plane bending, d^o in-plane bending, and n^o stretching

There are a few points worth noting: (a) There are no observable S-H stretching peaks at about 2500 cm⁻¹. This implies that, upon chemisorption, the S-H bond is activated due to the formation of a Pd-S bond. (b) The g(CH)/n(CH) intensity ratios are 0.97 for Pd-η⁷-S-H2Q and 1.41 for Pd-η¹-S-H2Q. This significant change confirms that the diphenolic ring adopts different orientations when chemisorbed on the Pd surface at low and high concentrations. (c) The presence of g(CH) and n(CH) vibrational modes from the aromatic ring indicates that the aromatic ring remained intact upon chemisorption.

The HREEL spectrum of chemisorbed DHOT from a 0.04-mM solution is shown in Figure 6. Two major differences from Figure 5 can be observed: (a) there are two C-H stretching peaks at ~ 3000 cm⁻¹, and (b) a less well-defined C-H bending peak at ~ 800 cm⁻¹ is present. Based on a Lorentzian function fitting method, two peaks at 2905 cm⁻¹ and 3048 cm⁻¹ are obtained for the C-H stretching peaks. These two peaks can be assigned to alkyl -CH2- and aromatic C-H stretching modes, respectively.^{23,24} The intensity ratio of I2905/I3048 was found to be 1.06. The close-to-unity ratio may be due to the fact that DHOT molecules are densely packed on Pd(111) surfaces such that only a small portion of the -CH2- is not shielded from the incident electrons. The broadened C-H bending peaks at ~800 cm⁻¹ can be attributed to steric effects within the closely packed adlayer. The diphenolic C-H stretching peaks for

DHT (5 mM DHT) and for DHOT are essentially identical (3043 cm^{-1} and 3048 cm^{-1} , respectively). This, of course, is expected since in both cases, the diphenolic ring is pendant.

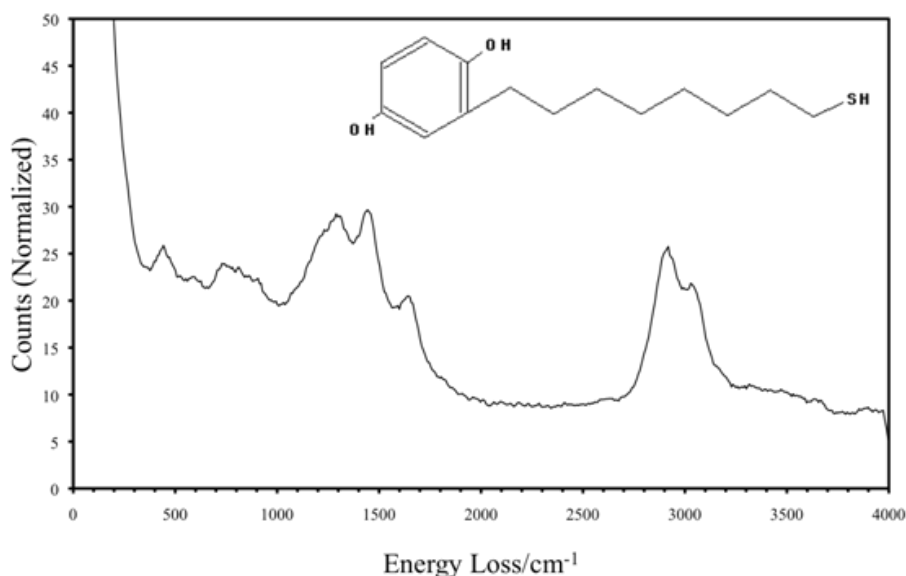


Figure 6. HREEL spectrum of chemisorbed DHOT on a Pd(111) surface from a 0.04-mM solution. Experimental conditions: incident beam energy = 3.67 eV; incidence and detection angles = 62° from surface normal; beam current = 55 pA.

CONCLUSION

The chemisorption of 2,5-dihydroxythiophenol (DHT) and 2-(8-mercaptooctyl)-1,4-benzenediol (DHOT) from aqueous solutions onto well-defined Pd(111) surfaces were studied by Auger electron spectroscopy (AES), low energy electron diffraction (LEED), high resolution electron energy-loss spectroscopy (HREELS), and electrochemistry (EC). Results validate that: (i) DHT is chemisorbed in two discrete orientations on the Pd surface depending on the aqueous solution concentrations; (ii) at low concentrations, DHT is oxidatively chemisorbed to the surface through the diphenol and mercapto groups as quinonoid and S moieties, respectively; (iii) at high concentrations, the molecule is

oxidatively coordinated only through the –SH group in a vertical S- η^1 orientation; (iv) iodine displaces the coordinated quinone ring causing it to be pendant; (v) by comparing the electrochemical activity of chemisorbed DHT and DHOT, it was found that interactions between DHT molecules on the Pd(111) surface are substrate-mediated.

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