Guaiacol Adsorption and Decomposition on Platinum

Emanuel V. Scoullos, Michelle S. Hofman, Yiteng Zheng, Denis V. Potapenko, Ziyu Tang, Simon G. Podkolzin, and Bruce E. Koel

Department of Chemical and Biological Engineering and Department of Chemistry, Princeton University, Princeton, New Jersey 08544, United States

Department of Chemical Engineering and Materials Science, Stevens Institute of Technology, Hoboken, New Jersey 07030, United States

Supporting Information

ABSTRACT: Guaiacol (2-methoxyphenol, \( \text{C}_6\text{H}_4(\text{OH})(\text{OCH}_3) \)) adsorption and reactions on a Pt(100) surface were studied with infrared reflection–absorption spectroscopy (IRAS) and temperature programmed desorption (TPD) measurements at different surface coverage values from 100 to 800 K. In addition, density functional theory (DFT) calculations were used to determine geometries, adsorption energies, and vibrational frequencies for adsorption structures. Depending on surface coverage, guaiacol formed one or two physisorbed states. At low coverage, a single state with a desorption peak at 225 K was observed. At high coverage, two physisorbed states were observed with desorption peaks at 195 and 225 K. At temperatures above 225 K, after the desorption of physisorbed layers, a dissociatively adsorbed structure, \( \text{C}_6\text{H}_4(\text{OCH}_3) + \text{H} \), was observed. Recombinative molecular guaiacol desorption was detected at 320 K. The dissociatively adsorbed structure was stable up to 337 K when C–O bonds began to break. Molecularly adsorbed guaiacol in horizontal (flat-lying) configurations bound through its benzene ring was not observed under all tested conditions. Similarities of vibrational spectra and desorption measurements for a Pt(100) surface in this study and a Pt(111) surface reported previously demonstrate that the obtained results are generally valid for low-index Pt crystal planes and, more importantly, for catalytic Pt nanoparticles.

1. INTRODUCTION

Adsorption and surface reactions of guaiacol (2-methoxyphenol, \( \text{C}_6\text{H}_4(\text{OH})(\text{OCH}_3) \)) are important in a wide range of applications, for example in biomass conversion, waste-water treatment, material science, climate change monitoring, and synthesis of biologically active compounds. In biomass conversion, more efficient technologies for processing lignocellulosic biomass into fuels and chemicals are needed to develop environmentally friendly and sustainable alternatives for the current use of fossil fuels. In one of the technologies, biomass is first converted using pyrolysis into a bio-oil, which is then upgraded by hydrodeoxygenation (HDO) to improve its stability and caloric value.

Since guaiacol is one of the major components of bio-oils, it can serve as a useful model chemical in the development of improved HDO processes. Guaiacol’s precursor compound, lignin, is a phenylpropane polymer with methoxy and hydroxyl substitutions. The hydroxyl group is situated para to the propyl group, and the methoxy group is situated ortho to the hydroxyl group. The presence of the hydroxyl and methoxy functional groups in guaiacol allows monitoring of hydrogenation reaction selectivities for both groups as well as for the benzene ring. The product distribution depends on the catalyst and reaction conditions. Although multiple guaiacol HDO studies evaluated several monometallic and bimetallic transition-metal catalysts, including Pt, Pd, Rh, Co–Mo, and Ni–Mo, molecular fundamentals of guaiacol adsorption and reactions on catalytic metal surfaces are not well understood.

Only recently have surface science studies begun to elucidate these fundamentals using well-defined model surfaces. A recent study compared adsorption of guaiacol on Pt(111) and Zn/Pt(111) surfaces with high-resolution electron energy loss spectroscopy (HREELS) and temperature programmed desorption (TPD). One of the main unresolved issues, however, remains the initial structure of chemisorbed guaiacol on Pt surfaces prior to decomposition, hydrogenation, and other reactions. Although spectroscopic results demonstrate that the guaiacol C–C bonds practically do not change on adsorption, previously proposed adsorption structures and reaction mechanisms assume that guaiacol is strongly adsorbed through its benzene ring. Such an adsorption mode should significantly change the C–C bond distances in the benzene ring and,
therefore, it is not consistent with the spectroscopic results. To resolve this inconsistency, this study evaluated multiple guaiacol adsorption structures with density functional theory (DFT) calculations and compared them to experimental results obtained with infrared reflection–absorption spectroscopy (IRAS) and TPD measurements on a Pt(100) surface. The combination of the experimental and computational results clarifies vibrational frequency assignments, identifies chemisorbed structures, and provides an improved interpretation of the guaiacol surface chemistry.

2. METHODS

2.1. Experimental Methods. All experiments were performed in a stainless steel ultrahigh vacuum chamber with a base pressure of $8 \times 10^{-11}$ Torr. The chamber was equipped with Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), TPD, and IRAS capabilities. All TPD experiments were performed with a shielded UTI 100C quadrupole mass spectrometer with the sample in line-of-sight of the ionizer. The TPD measurements were conducted with a heating rate of 3 K/s by monitoring 14 masses: 2, 15, 18, 27, 28, 29, 31, 42, 44, 78, 94, 108, 110, and 124 amu. IRAS measurements were carried out using a Bruker Vertex 70 IR spectrometer with a grazing incidence beam at 75° from the surface normal and a liquid nitrogen-cooled MCT detector. The spectrometer resolution was 2 cm$^{-1}$. The spectra were obtained by first adsorbing guaiacol at 100 K, then annealing to the indicated temperature at a ramp rate of 3 K/s (the same as in the TPD measurements), and finally rapidly cooling to 100 K. The spectra were collected by averaging 512 scans over a 5 min period at 100 K, with the background spectrum recorded from a clean surface.

The Pt(100) crystal was cleaned using 2 kV Ar$^+$ ion sputtering combined with annealing cycles at 1100 K. Additional oxygen treatments for several minutes at an O$_2$ pressure of $1 \times 10^{-7}$ Torr with the sample at 1100 K were used to eliminate residual carbon. This process produced a sharp (5 × 20) “hex” LEED pattern characteristic of the reconstructed (100) surface. Surface purity was verified with AES to ensure carbon and oxygen concentrations of less than 0.1%.

Guaiacol (Sigma-Aldrich, ≥98%) was transferred into a glass tube containing MolSieve 3A, which was used as a drying agent. The tube was attached to a gas-handling system. The guaiacol was further purified using several freeze–pump–thaw cycles until no visible gas bubbles were present. The purified guaiacol was introduced into the chamber via a stainless steel tube douser connected to a variable precision leak valve. The Pt(100) sample was cooled to 100 K using liquid nitrogen. Guaiacol decomposition during TPD experiments resulted in the formation of residual carbon on the surface. To remove this residual carbon, the crystal was annealed in oxygen and then in vacuum at 1100 K prior to each additional TPD experiment. Surface coverage values, $\theta$, were calculated based on the density of Pt atoms on a Pt(100) surface: 1.302 × $10^{15}$ atoms/cm$^2$.

An IR spectrum of guaiacol in the gas phase was obtained with a cell equipped with CaF$_2$ windows using a Bruker Vertex 70 IR spectrometer with a 2 cm$^{-1}$ spectrometer resolution. Prior to the measurements, the cell was evacuated with a molecular drag pump, and the background spectrum was taken of the evacuated cell. The spectrum of guaiacol vapor was taken by averaging 512 scans over a 5 min period.

An IR spectrum of guaiacol in the liquid phase was obtained using a Thermo Scientific Nicolet iN10 MX infrared imaging microscope. A droplet of guaiacol was placed on a clean microscope slide with a Au-sputtered surface for sample analysis. A background IR spectrum was recorded using an image of a dry section of the slide, and the liquid guaiacol IR spectrum was recorded afterward by moving the imaging microscope over a thin layer of liquid. The background and sample spectra were recorded with a 2 cm$^{-1}$ resolution.

2.2. Computational Methods. Adsorption of guaiacol on a Pt(100) surface was examined with DFT calculations using the DMol$^3$ code$^{19,20}$ in Materials Studio 2017 software by Dassault Systèmes BIOVIA. The Pt(100) surface was constructed using a $3 \times 3 \times 5$ periodic unit cell, which is shown in Figure 1 with adsorbed guaiacol molecules. The unit cell had $3 \times 3$ surface Pt atoms and 5 layers with a total of 45 Pt atoms. The unit cell was generated from a bulk crystal using the optimized Pt lattice constant of 0.3973 nm (within 1.2% of the 0.3924 nm experimental value) with a vacuum spacing of 4 nm in the c direction. Similarly constructed periodic surfaces with similar computational settings were previously used successfully for studying adsorption and reactions on metal surfaces.$^{21-25}$

The calculations used the double numerical with polarization (DNP) basis set and the generalized gradient-corrected PBE functional. Tightly bound core electrons for Pt were represented with semicore pseudopotentials. Reciprocal-space integration over the Brillouin zone was approximated through $k$-point sampling with a separation of 0.5 nm$^{-1}$ using the Monkhorst–Pack grid: 2 × 2 × 1. Convergence with respect to the number of $k$-points was tested by increasing their number for representative structures. The density mixing fraction of 0.1 with direct inversion in the iterative subspace (DIIS) and orbital occupancy were used. The orbital cutoff distance of 0.4 nm was set for all atoms.

The positions of the Pt atoms in the three top layers of the unit cell were optimized with adsorbed guaiacol during geometry optimizations, simulating surface relaxation after adsorption. The positions of the Pt atoms in the remaining two bottom layers were constrained at the bulk Pt positions, simulating the bulk crystal structure. Adsorption energies were calculated at 0 K without zero-point energy corrections using as a reference the sum of energies for the Pt(100) surface and an isolated guaiacol molecule calculated separately. Adsorption energies are reported as positive numbers, $-\Delta E_{ads}$. Adsorption energies for horizontal (flat-lying) molecularly adsorbed configurations and dissocia-
tively adsorbed \( (\text{C}_6\text{H}_4(\text{O})(\text{OCH}_3) + \text{H}) \) configurations are reported based on calculations with one guaiacol molecule adsorbed on the unit cell surface with \( 3 \times 3 \) Pt atoms (Figure 1a,c,d), which correspond to a 1/9 ML coverage. Adsorption energies for the tilted configuration are reported based on calculations with two guaiacol molecules adsorbed on the unit cell surface with \( 3 \times 3 \) Pt atoms (Figure 1b), which correspond to a 2/9 ML coverage. Vibrational frequency calculations were performed with a full Hessian matrix. All vibrational frequencies are reported as calculated, without any adjustments.

3. RESULTS

3.1. TPD of Guaiacol on Pt(100). Figure 2 shows a series of thermal desorption curves at different surface coverage values obtained with different exposures for molecular guaiacol \( (m/z = 124) \) adsorbed on Pt(100). At low coverages, up to 0.02 ML, a broad desorption feature from 225 to 320 K was observed. At higher coverages, an additional peak at 225 K was observed. At coverages above 0.11 ML, two peaks at 195 and 225 K with a broad tail up to 350 K were observed.

Figure 3 shows TPD curves for multiple masses for a single guaiacol coverage of 0.75 ML. In addition to the guaiacol desorption peaks at 195 and 225 K, hydrogen \( (\text{H}_2, m/z = 2) \) desorbs in multiple peaks at 230, 330, 395, 510 K, and in a broad feature extending to 675 K. These multiple peaks indicate increasing stages of hydrocarbon dehydrogenation. Methane \( (\text{CH}_4, m/z = 15) \) desorbs simultaneously with \( \text{H}_2 \) at 330 K, indicating that the dehydrogenation at this stage is accompanied by \( \text{O}−\text{CH}_3 \) bond scission. The mass of 15 was used for methane monitoring to avoid a possible contribution from oxygen with a mass of 16. Carbon monoxide \( (\text{CO}, m/z = 28) \) and formaldehyde \( (\text{CH}_2\text{O}, m/z = 29) \) desorb concurrently in a broad peak at 450 K, indicating significant guaiacol decomposition below this temperature. Small amounts of benzene \( (\text{C}_6\text{H}_6, m/z = 78) \) and phenol \( (\text{C}_6\text{H}_5\text{OH}, m/z = 94) \) desorb at 400 and 385 K, respectively.

3.2. IRAS of Guaiacol on Pt(100). Figure 4 shows an evolution of IRAS spectra from 100 to 575 K for an initial coverage of 0.45 ML of guaiacol on Pt(100). For comparison with the adsorption results in Figure 4 and as a reference for DFT frequency calculations, spectra for gas- and liquid-phase guaiacol were collected, and they are provided in Figure 5. The experimental IR vibrational frequencies for guaiacol in the gas

![Figure 2](image1.png)

**Figure 2.** TPD curves for increasing surface coverage of guaiacol \( (m/z = 124) \) adsorbed on Pt(100). Dosing conditions: 100 K. The insert shows the same spectra with a different scale.

![Figure 3](image2.png)

**Figure 3.** TPD curves for guaiacol adsorbed on Pt(100). Dosing conditions: 0.75 ML initial surface coverage, 100 K.

![Figure 4](image3.png)

**Figure 4.** Evolution of IRAS spectra as a function of temperature for guaiacol on Pt(100). Dosing conditions: 0.45 ML initial surface coverage, 100 K.

![Figure 5](image4.png)

**Figure 5.** IR spectra for gas- and liquid-phase guaiacol at 298 K. A calculated IR spectrum for an isolated guaiacol molecule (model for gas-phase guaiacol) is included for comparison. The IR peak positions are summarized in Table 1. The vibrational modes for the labeled peaks are illustrated with 3D animation in Figures S2–S5.
Table 1. Guaiacol IR Vibrational Frequencies, cm\(^{-1}\)

<table>
<thead>
<tr>
<th>Mode</th>
<th>Gas (Experimental)</th>
<th>Gas (Calculated)</th>
<th>Liquid (Experimental)</th>
<th>Pt(111) (Experimental)</th>
<th>Pt(100) (Experimental)</th>
<th>Pt(111) (Calculated)</th>
<th>Pt(100) (Calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu(C-H))</td>
<td>not observed</td>
<td>656</td>
<td>733</td>
<td>740</td>
<td>748</td>
<td>709</td>
<td></td>
</tr>
<tr>
<td>(\delta(C-CC) + \delta(COCH_3))</td>
<td>not observed</td>
<td>755</td>
<td>765</td>
<td>not observed</td>
<td>760</td>
<td>760</td>
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<tr>
<td>(\gamma(C-H))</td>
<td>not observed</td>
<td>852</td>
<td>834</td>
<td>830</td>
<td>839</td>
<td>890</td>
<td></td>
</tr>
<tr>
<td>(\delta(CCC) + \nu(O-CH_3))</td>
<td>1037</td>
<td>1030</td>
<td>1030</td>
<td>1010</td>
<td>1028</td>
<td>1010</td>
<td></td>
</tr>
<tr>
<td>(\delta(C-H) + \nu(O-CH_3))</td>
<td>1045, 1111</td>
<td>1052, 1101</td>
<td>1055, 1106</td>
<td>not observed</td>
<td>1043, 1112</td>
<td>1044, 1117</td>
<td></td>
</tr>
<tr>
<td>(\delta(C-H) + \nu(CH_3) + \delta(COCH_3))</td>
<td>1178, 1207</td>
<td>1167, 1184</td>
<td>1178, 1190</td>
<td>not observed</td>
<td>1178, 1209</td>
<td>1157, 1162</td>
<td></td>
</tr>
<tr>
<td>(\delta(C-H) + \nu(C-OH) + \nu(C-OCH_3))</td>
<td>1234, 1268</td>
<td>1245, 1284</td>
<td>1238, 1274</td>
<td>1250</td>
<td>1232, 1268</td>
<td>1247, 1279</td>
<td></td>
</tr>
<tr>
<td>(\nu(C=O) + \delta(COH))</td>
<td>1298</td>
<td>1310</td>
<td>1305</td>
<td>not observed</td>
<td>1306</td>
<td>1233</td>
<td></td>
</tr>
<tr>
<td>(\nu(C-C) + \delta(CH_3))</td>
<td>1355</td>
<td>1388</td>
<td>1350</td>
<td>not observed</td>
<td>1365</td>
<td>1365</td>
<td></td>
</tr>
<tr>
<td>(\nu(C-C) + \delta(CH_2))</td>
<td>1454, 1461, 1471</td>
<td>1450, 1475, 1509</td>
<td>1440, 1449, 1473</td>
<td>1430</td>
<td>1444, 1458, 1471</td>
<td>1411, 1435, 1443</td>
<td></td>
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<tr>
<td>(\nu(C-C))</td>
<td>1505, 1603</td>
<td>1523, 1610</td>
<td>1511, 1615</td>
<td>1550</td>
<td>1508, 1599</td>
<td>1468, 1573, 1595</td>
<td></td>
</tr>
<tr>
<td>(\nu(CH_3))</td>
<td>2852–2964</td>
<td>2993, 3052, 3095</td>
<td>2842–2964</td>
<td>2870</td>
<td>2842–2969</td>
<td>2943, 3017, 3087</td>
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</tr>
<tr>
<td>(\nu(C-H))</td>
<td>3009–3068</td>
<td>3101, 3116, 3143, 3171</td>
<td>3008–3069</td>
<td>3030</td>
<td>3007–3071</td>
<td>3096, 3105, 3118, 3131</td>
<td></td>
</tr>
<tr>
<td>(\nu(O-H))</td>
<td>3593</td>
<td>3723</td>
<td>3543</td>
<td>3300</td>
<td>3420 (not observed at 249 K)</td>
<td>N/A</td>
<td></td>
</tr>
</tbody>
</table>

*Peaks below 900 cm\(^{-1}\) were not observed for gas-phase guaiacol because of the transparency limit of the CaF\(_2\) IR cell windows. \(\delta\) — deformation, \(\nu\) — stretch, \(\gamma\) — wag, \(\rho\) — rock.

The peak at the dosing temperature of 100 K in Figure 4 is dominated by the peaks that are similar to those for gas- and liquid-phase guaiacol (Table 1 and Figure S5), and therefore, these peaks must be due to a physisorbed multilayer. The most prominent peaks at 100 K are at 748, 1268, and 1508 cm\(^{-1}\). The assignments for these and other experimental IR peaks were made using visualization of the DFT-calculated vibrational modes. The first peak at 748 cm\(^{-1}\) (733 cm\(^{-1}\) for liquid) is due to wagging of the H atoms in the benzene ring, \(\nu(C-H)\) (Figure S1). This peak and other peaks below 900 cm\(^{-1}\) were not observed in the gas-phase measurements (Table 1 and Figure S5) because of the transparency limit of the CaF\(_2\) windows in the IR cell. The second peak at 1268 cm\(^{-1}\) (1268 cm\(^{-1}\) for gas, 1274 cm\(^{-1}\) for liquid) is due to the in-plane bending of the C–H bonds in the benzene ring coupled with C–OH and C–OCH\(_3\) bond stretches, \(\delta(C-C) + \nu(C-OH) + \nu(C-OCH_3)\) (Figure S2). An additional frequency with a lower IR intensity at 1232 cm\(^{-1}\) (1234 cm\(^{-1}\) for gas, 1238 cm\(^{-1}\) for liquid) has the same vibrational assignment (Figure S3, Table 1). The last third peak at 1508 cm\(^{-1}\) (1505 cm\(^{-1}\) for gas, 1511 cm\(^{-1}\) for liquid) is mostly due to stretches of the C–C bonds in the benzene ring, \(\nu(C-C)\) (Figure S4). This vibrational assignment also has an additional frequency with a lower IR intensity at 1599 cm\(^{-1}\) (1603 cm\(^{-1}\) for gas, 1615 cm\(^{-1}\) for liquid) (Figure S5).

The small peak at 1710 cm\(^{-1}\) in Figure 4, which is not observed for gas- or liquid-phase guaiacol (Table 1, Figure S5), is likely due to adventitious CO adsorbed on fourfold Pt surface sites. The position of this peak matches the HREELS peaks at 1700–1720 cm\(^{-1}\) reported for CO adsorbed on benzene on Pt(111) when CO is forced to predominantly adsorb on hollow Pt surface sites.\(^\text{27}\)

Heating from 100 to 191 K increased intensities of all initial guaiacol IR peaks (Figure 4), despite desorption of some guaiacol evidenced by the TPD peak at 195 K in Figure 2. This IR intensity increase indicates an increased two-dimensional (2D) ordering of guaiacol molecules on the surface. Since no large relative intensity changes were observed, guaiacol molecules experienced only a small, if any, reorientation relative to the surface. The IR peak positions remained essentially the same. The only notable exception was the peak for the O–H bond stretching that narrowed and shifted from 3420 to 3400 cm\(^{-1}\), which can be attributed to a loss of some hydrogen bonding in the multilayer.

The spectrum at a higher temperature of 249 K in Figure 4 should be due only to chemisorbed species because the TPD results in Figure 3 demonstrate that physisorbed guaiacol desorbs at lower temperatures of 195 and 225 K. At 249 K, the IR peak at 3400 cm\(^{-1}\) was no longer observed (Figure 4), indicating scission of the O–H bond in guaiacol with the formation of C\(_6\)H\(_4\)O(OCH\(_3\)) and H surface species. As the positions of the remaining IR peaks practically did not change after the O–H bond scission, the molecular structure (bond lengths and angles) of the C\(_6\)H\(_4\)O(OCH\(_3\)) surface species must resemble the original guaiacol molecule in the physisorbed multilayer. Although the peak positions did not change, their relative intensities changed, signifying ordering of the C\(_6\)H\(_4\)O(OCH\(_3\)) species on the surface, in contrast with a mostly random orientation of guaiacol molecules in the multilayer. Specifically, the intensity of the peak at 1508 cm\(^{-1}\) due to stretches of the C–C bonds in the benzene ring, \(\nu(C-C)\), decreased relative to that of the peak at 748 cm\(^{-1}\) due to wagging of the H atoms in the benzene ring, \(\nu(C-H)\), demonstrating that the benzene ring became oriented on the surface.
On heating to 337 K, the IR spectrum changed more significantly (Figure 4). The intensities of the guaiacol peaks decreased due to further molecular guaiacol desorption evidenced by a broad TPD peak at about 320 K in Figure 3 and further guaiacol decomposition evidenced by the TPD peaks for CH₄ and additional H₂ at 330 K shown in the same Figure 3. The disappearance of the υ(O−CH₃) peak at 1043 cm⁻¹ at 337 K in Figure 4 confirms the scission of the O−CH₃ bond at a temperature between 249 and 337 K, leading to the formation of CH₃ surface species. The CH₃ species can disproportionate, forming CH₄ and H surface species as well as CH₂ and H₂ desorption products observed in the TPD experiment. Moreover, the decrease in intensities for the peaks at 1232 (Figure S3) and 1268 cm⁻¹ (Figure S2) for the δ(C−H) + υ(C−OH) + υ(C−OCH₃) vibrational modes indicates additional unselective cleavage of the C−O bond.

Molecularly or dissociatively (C₆H₅O(OCH₃) and H) adsorbed guaiacol structures were no longer observed in the spectra at higher temperatures of 391 and 575 K in Figure 4. These spectra are consistent with further decomposition and the formation of multiple decomposition products observed in the TPD experiment in Figure 3: H₂, CO, CH₂O, C₆H₆ (benzene), and C₆H₅OH (phenol).

**3.3. DFT-Calculated Adsorption Structures.** Molecular and dissociative guaiacol adsorption on Pt(100) was examined on atop, bridge, and fourfold sites at two surface coverage values: 1/9 and 2/9 ML. In addition, different orientations of a guaiacol molecule relative to surface Pt−Pt bonds were examined for each adsorption site for horizontal (flat-lying) configurations at the low coverage value of 1/9 ML. The evaluated twelve possible horizontal configurations are shown schematically in Figure 6.

![Figure 6](https://example.com/figure6.png)

**Figure 6.** Evaluated adsorption sites and guaiacol orientations for horizontal (flat-lying) configurations on Pt(100). The first angle indicates the orientation of the benzene ring relative to Pt surface bonds. The second angle indicates the orientation of the OH and OCH₃ substituents. The evaluated structures prior to optimization are shown schematically to distinguish them from the fully optimized structures in Figures 1 and 7. The adsorption energies are reported for stable structures after geometry optimization.

The adsorption site is defined based on the position of the center of the benzene ring. The orientation of an adsorbed guaiacol molecule is described with two angles. The first angle indicates the orientation of the benzene ring relative to Pt surface bonds. When two C−C bonds in the benzene ring are parallel to Pt−Pt surface bonds, this orientation is designated as R₀°. The second angle indicates the orientation of the C−C bond for the C atoms with OH and OCH₃ substituents relative to Pt surface bonds. When this C−C bond is parallel to Pt−Pt surface bonds, this orientation is designated as R₀°. As an example, the configuration in Figure 6a is designated as fourfold 0° R₀° because the center of the benzene ring is over a fourfold site, two C−C bonds in the benzene ring are parallel to Pt−Pt surface bonds, and the C−C bond for the C atoms with substituents is also parallel to Pt−Pt surface bonds.

In all horizontal configurations, guaiacol adsorbs through its benzene ring, with the ring plane being parallel to the surface. The configurations on the fourfold site with adsorption energies of 230−241 kJ/mol (Figure 6a−c) are significantly more stable than the configurations on the bridge site with adsorption energies of 122−153 kJ/mol (Figure 6g−l). The configurations on the atop site (Figure 6d−f) are not stable and converge to the same orientations but on the fourfold site (Figure 6a−c) after geometry optimization. The fourfold 0° R₀° is the most energetically preferable configuration with an adsorption energy of 241 kJ/mol. In addition to Figure 6b, this configuration is also shown in a 3D view in Figure 1a as well as with side and top projection views in Figure 7a. The geometry details for the most stable configuration on the bridge site (bridge 0° R₀° in Figure 6g) with an adsorption energy of 153 kJ/mol are provided in Figure 7b.

In the horizontal adsorption configurations, an adsorbed guaiacol molecule has a large surface “footprint”. As a result, the horizontal configurations become impossible due to steric constraints with increasing surface coverage. For example, the most stable fourfold 0° R₀° configuration in Figure 7a calculated at 1/9 ML coverage becomes unstable and converts after geometry optimization into a tilted configuration in Figure 7c at an increased coverage of 2/9 ML due to lateral repulsive interactions with neighboring adsorbed guaiacol molecules. Although the adsorption energy of 91 kJ/mol for this tilted configuration is lower than 122−241 kJ/mol for the horizontal configurations (Figure 6), guaiacol binds through not six but only two C atoms in the benzene ring to two Pt atoms (bridge site), significantly reducing the surface “footprint” and, thus, allowing for the increased surface coverage.

Similar to molecularly adsorbed guaiacol, two structures were identified for high and low surface coverage values for dissociatively adsorbed guaiacol after scission of the O−H bond, C₆H₅O(OCH₃) and H. At low coverage, the C₆H₅O(OCH₃) fragment bonds through the O atom from the dissociated hydroxyl group and the neighboring C atom without the methoxy group (Figure 7e). The bonding O and C atoms each form a bond with a separate Pt atom, adsorbing on a bridge site. The plane of the benzene ring is almost parallel to the surface, and the corresponding “footprint” is similar to that for the molecularly adsorbed horizontal configurations in Figure 7a,b. The adsorption energy of 110 kJ/mol relative to gas-phase guaiacol is significantly lower than that for the horizontal configurations in Figure 6, but greater than 91 kJ/mol for the tilted configuration at high coverage in Figure 7c.

The second configuration for the C₆H₅O(OCH₃) fragment is tilted (Figure 7d), similar to the molecularly adsorbed tilted
configuration in Figure 7c. In this tilted configuration, the hydrocarbon binds only through the O atom from the dissociated hydroxyl group to a single Pt atom (atop site). This tilted dissociatively adsorbed guaiacol with a smaller surface “footprint” should be preferable at high coverage to the nearly horizontal configuration with binding through the O and C atoms in Figure 7e, despite a lower adsorption energy. The calculated adsorption energy of 53 kJ/mol for the molecularly adsorbed tilted configuration, the shorter bonds are significantly by more than 150 cm⁻¹, from 1505 and 1603 cm⁻¹ in the gas phase (calculated 1523 and 1610 cm⁻¹, Table 1) to 1419, 1431, and 1440 cm⁻¹ (Table 2). In contrast, since the OH and OCH₃ fragments are affected less by the hydrocarbon–surface binding, their vibrational frequencies are predicted to remain closer to those in an isolated molecule, mostly shifting by 20–70 cm⁻¹. For example, the in-plane bending of the ring C–H bonds coupled with stretches of C–OH and C–OCH₃ bonds, δ(C–H) + ν(C–OH) + ν(C–OCH₃), is predicted to change from 1234 and 1268 cm⁻¹ in the gas phase (1245 and 1284 cm⁻¹ calculated, Table 1) to 1224 and 1330 cm⁻¹, respectively. Since the two additional configurations on the fourfold site, 0° R0° in Figure 6a and 0° R120° in Figure 6c, have similar geometries as that of the most stable fourfold 0° R60° configuration in Figure 6b, their frequencies are also similar, mostly within 20 cm⁻¹ (Table 2).

In the most energetically preferable fourfold 0° R60° configuration, two C–C bonds in the benzene ring are shorter than the remaining four C–C bonds. The shorter bonds are shown as double bonds in Figure 7a. In contrast, all six C–C bonds in the benzene ring are similar in the bridge 0° R0° configuration. This is illustrated with the classic Kekule structure with alternating C≡C double bonds in Figure 7b. These bonding differences cause the following main differences in

![Figure 7. Guaiacol structures on Pt(100) obtained with DFT calculations: (a) fourfold 0° R60° is the overall most energetically preferable structure. (b) Bridge 0° R0° is the most stable horizontal structure on a bridge site. (c) Tilted configuration at high surface coverage with adsorption through two C atoms in the benzene ring. (d) Dissociatively adsorbed structure, C₆H₄O(OCH₃) and H, with the hydrocarbon fragment bonding through an O atom to a single Pt atom (atop site) is preferable due to steric effects at high surface coverage. (e) Dissociatively adsorbed structure, C₆H₄O(OCH₃) and H, with the hydrocarbon fragment bonding through O and C to two separate Pt atoms (bridge site) is energetically preferable at low surface coverage. Side (upper row) and top (lower row) projection views. Only two top Pt layers are shown for clarity.](Image)

<table>
<thead>
<tr>
<th>Table 2. Calculated Guaiacol IR Vibrational Frequencies (cm⁻¹) for the Horizontal (Flat-Lying) Adsorbed Structures on the Fourfold Site in Figure 6a–c</th>
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<tr>
<td>γ(C–H)</td>
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<tr>
<td>δ(CCC) + δ(COCH₃)</td>
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<tr>
<td>γ(C–H)</td>
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<td>δ(CCC) + υ(O–CH₃)</td>
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<tr>
<td>δ(C–H) + υ(CH₃)</td>
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<td>δ(C–H) + υ(CH₄) + δ(COH)</td>
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<td>υ(C–H)</td>
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<tr>
<td>υ(O–H)</td>
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</table>
The tilted configuration in Figure 7c is even less strongly bound than the horizontal configuration on the bridge site in Figure 7b. Instead of bonding through the whole benzene ring, only two C atoms are bound to the surface. As a result, the molecular structure and vibrational frequencies for the tilted configuration are closer to those for an isolated molecule. The frequencies for stretches of the C–C bond, υ(C–C), and wagging of the H atoms in the benzene ring, γ(C–H), are calculated to shift by less than 60 cm⁻¹ (Table 3). The other characteristic IR peaks for δ(C–H) + υ(C–OH) + υ(C–OCH₃) vibrational modes change less than 30 cm⁻¹ for the bridge configuration on the bridge site in Figure 7c compared with up to 62 cm⁻¹ for the fourfold site (Table 2).

In the dissociatively adsorbed structure bound through O and C atoms in Figure 7e, the benzene ring is less perturbed than in the tilted molecular configuration in Figure 7c because only one C atom is bound to the surface. However, bonding through the O atom causes additional bond distance and angle changes. Consequently, the frequency shifts for this structure are different than those for the tilted molecular configuration but their magnitude is similar. Specifically, the frequencies for the C–C bond stretches in the benzene ring, υ(C–C), and wagging of the H atoms in the benzene ring, γ(C–H), are calculated to shift by less than 50 cm⁻¹ (Table 3). The other characteristic IR peaks for δ(C–H) + υ(C–OH) + υ(C–OCH₃) are calculated to shift even less, by less than 25 cm⁻¹ (Table 3).

The dissociatively adsorbed structure bonded only through the O atom in Figure 7d is least perturbed compared to an isolated guaiacol molecule. The only difference is that the H atom in the OH group is replaced by a Pt surface atom. As a result, except for υ(O–H), which is not present, its vibrational frequencies are close to those of gas- and liquid-phase guaiacol (Table 1).

### 4. DISCUSSION

At the dosing temperature of 100 K, guaiacol forms physisorbed layers because the IRAS spectrum at this temperature in Figure 4 is practically identical to the IR spectrum of liquid guaiacol at room temperature in Figure 5 and because the initial desorption peaks for molecular guaiacol in TPD measurements at 195 and 225 K in Figure 2 indicate weak physisorption binding. The TPD peak at 195 K observed for coverage values above 0.30 ML must be from a physisorbed multilayer. The TPD peak at a higher temperature of 225 K, which is observed for all coverage values, must be from a physisorbed layer that is closer to the surface and, therefore, is likely more ordered and, thus, more strongly physisorbed. The increased 2D ordering of the physisorbed layer close to the surface, which is expected due to hydrogen bonding, is evidenced by the increase of the IR peak intensities at 191 K compared to those at 100 K at 0.45 ML in Figure 4, even though some guaiacol desorbed between 100 and 191 K. These two physisorbed layers were previously reported for adsorption of guaiacol on Pt(111).

After the desorption of all physisorbed layers at 225 K, a transformation of the remaining chemisorbed layer occurs. The O–H bond scission in the chemisorbed guaiacol occurs at a temperature below 240 K as evidenced by the evolution of H₂ at 240 K in the TPD experiment in Figure 3. The O–H bond scission must occur at a temperature below 240 K because the evolution of H₂ after adsorption on a clean Pt(100) was previously observed at a similar temperature. Therefore, the H₂ evolution at 240 K in Figure 3 is limited by H₂ desorption, not by the O–H bond scission. The disappearance of the broad peak at 3420 cm⁻¹ due to the O–H bond stretch in the IRAS spectrum at 249 K in Figure 4 confirms the O–H bond scission below this temperature. Since the positions of all other IRAS peaks remain unchanged at 249 K, H₂ atoms in the methyl group and the benzene ring must be unaffected. The H₂ evolution at 240 K, therefore, is due exclusively to the scission of the O–H bond. As no new IRAS peaks are observed at 249 K, hydrogenation of the benzene ring by surface hydrogen and any other reactions leading to the formation of new surface species can be ruled out. The molecular structure of the surface hydrocarbon fragment after the O–H bond scission remains intact. Therefore, the only structure that is consistent with the IRAS spectrum at 249 K in Figure 4, which is similar to the gas- and liquid-phase spectra in Figure 5 except for the absence of the υ(O–H) peak, is dissociatively adsorbed guaiacol, C₆H₄O(OCH₃) + H.

<table>
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<th>Table 3. Calculated Guaiacol IR Vibrational Frequencies (cm⁻¹) for the Adsorbed Structures in Figure 7b,c,e</th>
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<td>Structure</td>
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<td>γ(C–H)</td>
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<tr>
<td>δ(CCC) + δ(COCH₃)</td>
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<td>υ(C–H)</td>
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<td>δ(CCC) + δ(O–CH₃)</td>
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<td>δ(C–H) + δ(CH₃) + δ(COH)</td>
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<tr>
<td>δ(C–H) + δ(C–OH) + υ(C–OCH₃)</td>
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<td>δ(C–H) + δ(COH)</td>
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<td>υ(C–C) + δ(CH₃)</td>
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<td>υ(C–H)</td>
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<tr>
<td>υ(O–H)</td>
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</table>

The DFT calculations identify two structures for dissociatively adsorbed guaiacol. The first structure is weakly bonded only through the O atom that is missing the H atom in Figure 7d. The surface bonding through the O atom for the C6H4O-(OCH3)2 structure is similar to that of cyclohexanone on Pt.30 The second structure is more strongly bonded through the same O atom and, in addition, through a C atom in the benzene ring (Figure 7e). Since the IRAS spectrum for chemisorbed species at 249 K is almost identical to the spectra of molecular guaiacol in the gas and liquid phases in Figure 5, the weakly adsorbed structure bonded only through the O atom in Figure 7d must be the dominant surface species. In this structure, the H atom in the OH group is substituted by a surface Pt atom, and its molecular structure remains mostly unchanged. Consequently, the calculated frequencies are close to those for gas- and liquid-phase guaiacol (Table 1). However, since the second dissociatively adsorbed structure in Figure 7e is more energetically preferable, it is likely that it is also present as a minority species, especially at higher temperatures when the surface coverage decreases because it has a higher surface “footprint”. The tilted molecularly adsorbed guaiacol in Figure 7c may also be present as a minority species because only relatively small frequency shifts compared to gas-phase guaiacol are calculated for this structure (Table 3). We note that tilted configurations have not been previously considered for guaiacol adsorption on Pt. The tilted configuration in Figure 7c with binding through two C atoms in the benzene ring on a Pt–Pt bridge site is the first reported structure.

Since the weakly bonded dissociatively adsorbed guaiacol in Figure 7d is less energetically stable than the tilted molecularly adsorbed guaiacol in Figure 7c, recombination of the dissociatively adsorbed structure into the molecular species is thermodynamically preferable. Therefore, a broad desorption feature for molecular guaiacol from 250 to 350 K with a peak at about 320 K observed in TPD measurements in Figure 2 can be attributed to recombinative desorption. Thus, weakly bonded dissociatively adsorbed guaiacol observed at 249 K partially desorbs molecularly and partially decomposes at higher temperatures.

Importantly, under no conditions, strongly adsorbed horizontal (flat-lying) guaiacol structures bonded through the benzene ring (Figure 7a,b) are observed. The bonding through the benzene ring should change the characteristic vibrational frequencies significantly (Tables 2 and 3) compared to those for gas-phase guaiacol (Table 1). The calculated large frequency shifts for the horizontal guaiacol structures are in agreement with reflection absorption infrared spectroscopy (RAIRS) and electron energy loss spectroscopy (EELS) results for benzene adsorption on Pt at low coverage, which are conclusively interpreted as being due to horizontal (flat-lying) benzene adsorbed through its ring.31–33 The vibration with stretches of the C–C bonds, \( \nu(C-C) \), shifts from 1310 cm\(^{-1} \) for gas-phase benzene to 1420–1480 cm\(^{-1} \) when adsorbed on Pt, a shift of more than 100 cm\(^{-1} \).32,34 Similarly, wagging of the H atoms in the benzene ring, \( \delta(C-H) \), shifts from 673 cm\(^{-1} \) for gas-phase benzene to 829–830 and 900–920 cm\(^{-1} \) on Pt, corresponding to shifts of more than 150 cm\(^{-1} \). Since no frequency shifts are observed for adsorbed guaiacol (Table 1 and Figure 4), all strongly adsorbed horizontal structures (Figure 6) can be completely ruled out under all tested conditions.

At temperatures above 249 K, the weakly bonded dissociatively adsorbed guaiacol begins to decompose as evidenced by significant changes in the IRAS spectrum at 391 K in Figure 4 and by the evolution of decomposition products in the TPD experiment in Figure 3. The simultaneous evolution of \( \Delta_2 \) and \( \Delta_4 \) at 330 K indicates scission of the O–C\(_2\) bond, which is confirmed by the decrease of the IRAS peak intensities of the \( \nu(CH_3) \) modes at 2840–2969 cm\(^{-1} \) and the \( \delta(CH_3) \) mode at 1444, 1458, 1471 cm\(^{-1} \). The TPD \( \Delta_2 \) peak at 395 K is likely due to dehydration of CH\(_3\) on the surface because CH\(_3\) was reported to be unstable on Pt(111) at this temperature.36 The C\(_{ring}\)–O bonds also begin to split, as evidenced by significant increases in the intensities of the IRAS peaks at 2033 and 1823 cm\(^{-1} \) due to CO adsorbed on, respectively, atop and bridge Pt sites.37 The scission of the C\(_{ring}\)–O bonds is additionally evidenced by the evolution of phenol at 385 K and benzene at 400 K in the TPD experiment in Figure 3.

Above 400 K, decomposition proceeds further, and carbon monoxide and formaldehyde decomposition products desorb concurrently at 450 K (Figure 3). At even higher temperatures, only H\(_2\) evolution from dehydrogenation of hydrocarbon surface fragments is detected as a TPD peak at 510 K and as a broad desorption feature up to 675 K. The dehydrogenation reactions ultimately produce surface carbon.

The conclusions that guaiacol initially adsorbs as a physisorbed multilayer, then becomes dissociatively adsorbed as C\(_6\)H\(_4\)O(OCH\(_3\)) + H surface species, and proceeds to decompose without forming strongly bonded horizontal configurations are not limited to the evaluated Pt(100) surface. Since similar vibrational spectra and TPD results were reported for a Pt(111) surface,17 these conclusions are generally valid for low-index Pt crystal planes and, more importantly, for catalytic Pt nanoparticles.

### 5. Conclusions

Depending on the surface hydrocarbon coverage, guaiacol forms one or two physisorbed layers on Pt(100). At lower coverages, there is only one physisorbed layer that desorbs at 225 K. At higher coverages, another less strongly bound physisorbed layer forms that desorbs at 195 K. After desorption of the physisorbed layers, a chemisorbed layer is observed that has already undergone a transformation due to O–H bond scission. This transformation is evidenced by the disappearance of the O–H bond stretch in the vibrational spectra and by the evolution of H\(_2\) in the TPD measurements. Therefore, the decomposition of guaiacol on Pt starts with O–H bond scission. As the positions of the remaining vibrational peaks do not change, the formed structure was assigned to the weakly bonded dissociatively adsorbed species, C\(_6\)H\(_4\)O(OCH\(_3\)) + H. In this structure, the dissociated H atom is substituted by a surface Pt atom, and most of the bond distances and angles in the C\(_6\)H\(_4\)O(OCH\(_3\)) fragment remain similar to those in a guaiacol molecule. A more strongly bound dissociatively adsorbed structure bonded through O and C atoms and a tilted molecularly adsorbed guaiacol may be present as minority species because their vibrational spectra are calculated to be similar.

The strongly bound horizontal (flat-lying) molecular guaiacol configurations adsorbed through the benzene ring were not detected under all experimental conditions because shifts of more than 100 cm\(^{-1} \) are expected for their characteristic vibrational frequencies while essentially no experimental frequency shifts were observed.

Similarities of the vibrational spectra and TPD results for the Pt(100) surface in this study and for a Pt(111) surface reported previously demonstrative that these results are generally valid for low-index Pt crystal planes. Therefore, the conclusions of the
absence of strongly bound horizontal molecular guaiacol configurations and the presence of a dissociatively adsorbed species, C₆H₆O(ΟCH₃) + H, as the main chemisorbed structure also apply to catalytic Pt nanoparticles with surfaces dominated by low-index crystal planes.

**ASSOCIATED CONTENT**

 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b06555.

Figures S1-S5: 3D animation of characteristic vibrational modes for guaiacol (PDF)

Figure S1: wagging of the H atoms in the benzene ring, \( \gamma(C-H) \), 733 cm\(^{-1} \) for liquid, 748 cm\(^{-1} \) on Pt(100) (GIF)

Figure S2: in-plane bending of the C-H bonds in the benzene ring coupled with C-OH and C-ΟCH₃ bond stretches, \( \delta(C-H) + \nu(C-OH) + \nu(C-ΟCH₃) \), 1268 cm\(^{-1} \) for gas, 1274 cm\(^{-1} \) for liquid, and 1268 cm\(^{-1} \) on Pt(100) (GIF)

Figure S3: in-plane bending of the C-H bonds in the benzene ring coupled with C-OH and C-ΟCH₃ bond stretches, \( \delta(C-H) + \nu(C-OH) + \nu(C-ΟCH₃) \), 1234 cm\(^{-1} \) for gas, 1238 cm\(^{-1} \) for liquid, and 1232 cm\(^{-1} \) on Pt(100) (GIF)

Figure S4: stretches of the C-C bonds in the benzene ring, \( \nu(C-C) \), 1505 cm\(^{-1} \) for gas, 1511 cm\(^{-1} \) for liquid, and 1508 cm\(^{-1} \) on Pt(100) (GIF)

Figure S5: stretches of the C-C bonds in the benzene ring, \( \nu(C-C) \), 1603 cm\(^{-1} \) for gas, 1615 cm\(^{-1} \) for liquid, and 1599 cm\(^{-1} \) on Pt(100) (GIF)

**AUTHOR INFORMATION**

Corresponding Authors
*E-mail: Simon.Podkolzin@Stevens.edu (S.G.P.).
*E-mail: bkoel@princeton.edu (B.E.K.).

ORCID

Simon G. Podkolzin: 0000-0002-9536-7176
Bruce E. Koel: 0000-0002-0332-4991

Author Contributions

E.V.S. and M.S.H. contributed equally to this paper.

Notes

The authors declare no competing financial interest.

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**REFERENCES**


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(30) Lim, J.; Welch, L. A.; Olivas, A.; Podkolzin, S. G.; Koel, B. E. Adsorption and Decomposition of Cyclohexanone (C_6H_{10}O) on Pt(111) and the (2×2) and (\sqrt{3}×\sqrt{3})R30°-Sn/Pt(111) Surface Alloys. *Langmuir* 2010, 26, 16401–16411.


