

# Adsorption and Reaction of Maleic Anhydride on Mo(110), Monolayer Pd(111)/Mo(110), and Multilayer Pd(111)/Mo(110)

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The adsorption and reaction of maleic anhydride and deuterated maleic anhydride on Mo(110), monolayer Pd/Mo(110), and multilayer Pd(111)/Mo(110) surfaces have been studied using temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS). Maleic anhydride adsorbs irreversibly on the Mo(110) surface at 100 K. Heating to 1200 K yields adsorbed carbon ( $C_{ads}$ ) and gas-phase CO and  $H_2$ . In contrast, the adsorption of maleic anhydride on monolayer Pd(111)/Mo(110) and multilayer Pd(111)/Mo(110) surfaces is largely reversible with the chemisorbed maleic anhydride desorbing at 365 and 375 K, respectively. Approximately 15% of the chemisorbed maleic anhydride decomposes upon heating to 400 K, forming CO,  $CO_2$ , and  $C_2H_2$ ;  $C_2H_2$  further dehydrogenates upon heating to  $C_{ads}$  and gas-phase  $H_2$ . The HREELS measurements indicate that maleic anhydride is bonded to multilayer Pd(111)/Mo(110) through the olefin bond in a di- $\sigma$  configuration, while on monolayer Pd(111)/Mo(110), the maleic anhydride is bonded to the surface through the olefin via a  $\pi$ -bond. On the Mo(110) surface, maleic anhydride is bonded to the surface through the ring oxygen with the molecular plane perpendicular to the surface. As a result of this modified adsorption geometry, the carbonyl stretching mode is red-shifted  $\sim 150\text{ cm}^{-1}$  on the monolayer Pd(111)/Mo(110) surface, unshifted on the multilayer Pd(111)/Mo(110) surface, and blue-shifted by  $\sim 100\text{ cm}^{-1}$  on the Mo(110) surface.

## 1. Introduction

Monolayer palladium ( $Pd_{1ML}$ ) supported on early transition metals often displays vastly modified properties with respect to its bulk counterpart. These unique properties of the monolayer have stimulated a number of recent studies on this system.<sup>1–17</sup> However, most of these investigations have addressed the adsorption and reaction of CO and  $H_2$  on  $Pd_{1ML}$ . Recently, Koel and co-workers have extended these studies on Pd/Ta(110) to other molecules such as  $C_2H_2$ ,  $C_2H_4$ ,<sup>15</sup> and NO.<sup>17</sup> A decreased binding energy of ethylene was found on  $Pd_{1ML}/Ta(110)$  relative to bulk Pd, consistent with previous data for CO and  $H_2$ .<sup>1–14</sup> However, for acetylene, the bonding on  $Pd_{1ML}/Ta(110)$  was found to be essentially identical to that for bulk Pd. This similarity was attributed to the strong interaction between acetylene and monolayer Pd which

rehybridizes the perturbed monolayer Pd back to its bulk electronic structure.<sup>15</sup>

The growth and behavior with respect to annealing of Pd on Mo(110) has been studied by Park et al.<sup>18</sup> using Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), and work function measurements. At monolayer or submonolayer coverages, Pd forms a pseudomorphic structure with no indication of alloy formation. At higher coverages, Pd grows in a layer-by-layer (Frank-van der Merwe) mode at room temperature. At higher temperatures, Pd forms a single pseudomorphic layer followed by 3D clustering in the second and subsequent layers (Stranski–Krastanow growth mode). Annealing the layer-by-layer structure formed by the deposition of Pd at room temperature to 600 K also leads to agglomeration of the second and subsequent Pd layers. Significant alloying of Pd with Mo via diffusion of the substrate Mo into the Pd overlayer also has been found; however, even with this alloying, measurements indicate that the surface consists entirely of Pd. Pd coverages of  $>12\text{ ML}$  grown at room temperature are resistant to 3D agglomeration even with a 900 K anneal, likely because of kinetic considerations. Such relatively thick Pd overlayers show a sharp hexagonal LEED pattern, suggesting epitaxial growth of a Pd(111)-like surface.

Commercially the production of maleic anhydride is exceeded only by acetic and phthalic anhydride.<sup>19</sup> The industrial production of maleic anhydride is based on the selective oxidation of either butane or benzene over a vanadium oxide catalyst.<sup>19</sup> In addition to other commercial applications, maleic anhydride also is utilized as a precursor in the commercial production of tetrahydrofuran. In this process, the conversion is carried out on a carbon-supported, Pd/Re bimetallic catalyst. Despite the importance of this commercial process, no studies prior to those in our laboratories of this system utilizing surface science techniques have been carried out. In an effort to

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understand the chemistry of this important bimetallic catalytic process, previous studies in our laboratories have addressed the adsorption and reaction of maleic anhydride and tetrahydrofuran on various Pd/Re bimetallic surfaces using temperature-programmed desorption (TPD), AES, XPS and ion scattering spectroscopy (ISS).<sup>20</sup> In this paper, we report complementary studies of maleic anhydride adsorption and reaction on various Pd/Mo(110) bimetallic surfaces. To conserve space, the Pd monolayer on Mo(110) and the epitaxially grown Pd multilayer on Mo(110) will be referred to as Pd<sub>1ML</sub>/Mo(110) and Pd(111)/Mo(110), respectively, in the following discussions.

## 2. Experimental Section

The experiments were carried out in an ultrahigh vacuum (UHV) chamber (base pressure  $<1 \times 10^{-10}$  Torr) that has been described in detail previously.<sup>21</sup> Briefly, the UHV chamber was equipped with capabilities for high-resolution electron energy loss spectroscopy (HREELS), AES, LEED, and TPD. HREELS spectra were acquired with a primary energy of 3 eV and a typical resolution of 60  $\text{cm}^{-1}$ . TPD measurements were carried out using a quadrupole mass spectrometer (QMS) in line-of-sight with the sample surface with a linear heating rate of  $\sim 5$  K/s. To avoid electron beam damage to the adsorbate, the sample was biased at  $-100$  V with respect to the QMS ionizer during the TPD experiments. The sample could either be resistively heated to 1500 K or to 2200 K using an e-beam assembly; the temperature was measured using a W-5% Re/W-26% Re thermocouple spot-welded onto the sample's edge. The Mo(110) crystal was cleaned by annealing in  $2 \times 10^{-8}$  Torr  $\text{O}_2$  while heating at 1200 K; the sample was subsequently flashed to 2000 K. This procedure was repeated several times until no contamination was detectable with AES.

The palladium source used for deposition consisted of a 0.25 mm Pd wire (99.997%, Johnson Matthey Chemical Limited) wrapped around a tungsten filament. The Pd source was extensively outgassed prior to evaporation. A QMS in a line-of-sight configuration was used to monitor the Pd flux, which was maintained approximately at 1 ML/min. The pressure during evaporation was never allowed to exceed  $3 \times 10^{-10}$  Torr. The Pd coverage was calibrated using TPD and AES as described previously.<sup>10</sup>

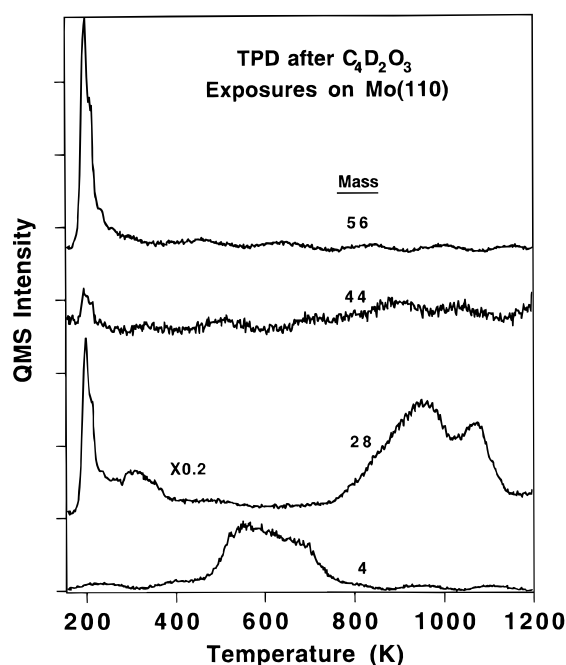
The maleic anhydride (Aldrich, 99%) and deuterated maleic anhydride (Matheson, 98.35 atom % D) were used after several freeze-pump-thaw cycles in the vacuum manifold. The maleic anhydride was dosed using a directional gas dose; the exposures are presented in units of Langmuir (1 Langmuir =  $1 \times 10^{-6}$  Torr s) without correction for the local pressure enhancement and gauge sensitivity.

## 3. Results

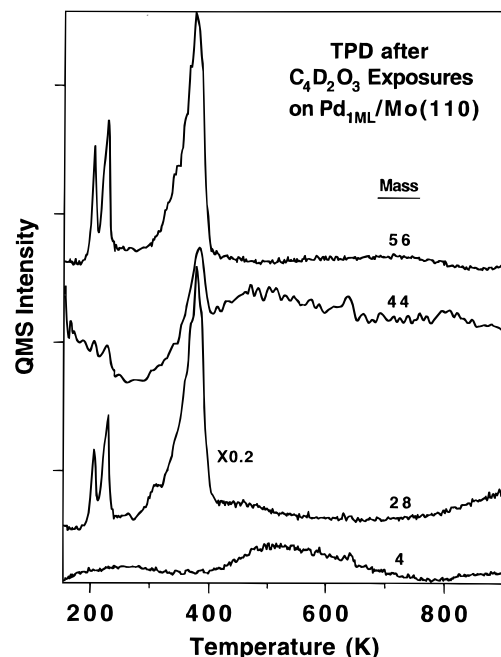
### 3.1. Temperature Programmed Desorption (TPD).

TPD spectra acquired subsequent to the adsorption of deuterated and nondeuterated maleic anhydride show similar results with no apparent isotope effect. Masses 2, 18, 26, 28, 32, 44, and 54 were monitored for the nondeuterated maleic anhydride. From the various surfaces studied,  $\text{H}_2$ , CO,  $\text{CO}_2$ , and molecular maleic anhydride were the only desorption products. Figures 1–3 show the TPD spectra of  $\text{D}_2$ , CO,  $\text{CO}_2$ , and molecular maleic anhydride acquired subsequent to the adsorption of deuterated maleic anhydride onto Mo(110), Pd<sub>1ML</sub>/Mo(110), and Pd(111)/Mo(110), respectively.

For the Mo(110) surface,  $\text{D}_2$  and CO are the major gas-phase desorption products. In addition, molecular desorption from multilayer maleic anhydride is seen near 200 K. The  $\text{D}_2$  TPD spectra are dominated by two broad peaks between 470 and 770 K. The TPD spectrum of CO



**Figure 1.** TPD spectra of  $\text{D}_2$ , CO,  $\text{CO}_2$ , and maleic anhydride desorption after dosing deuterated maleic anhydride at 100 K on the Mo(110) surface.

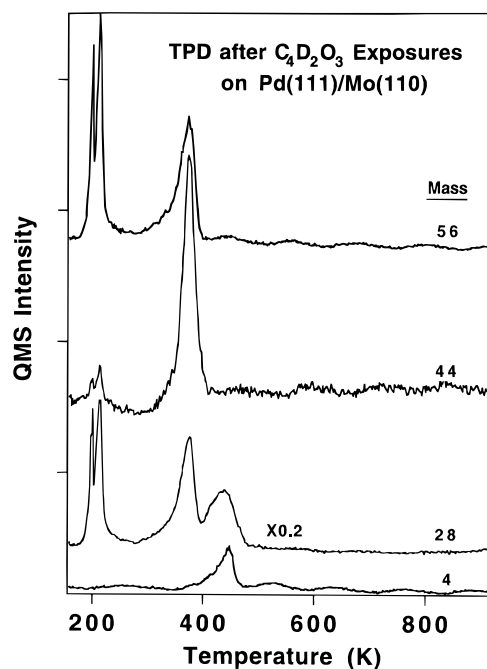


**Figure 2.** TPD spectra of  $\text{D}_2$ , CO,  $\text{CO}_2$ , and maleic anhydride after dosing deuterated maleic anhydride at 100 K on the Pd<sub>1ML</sub>/Mo(110) surface.

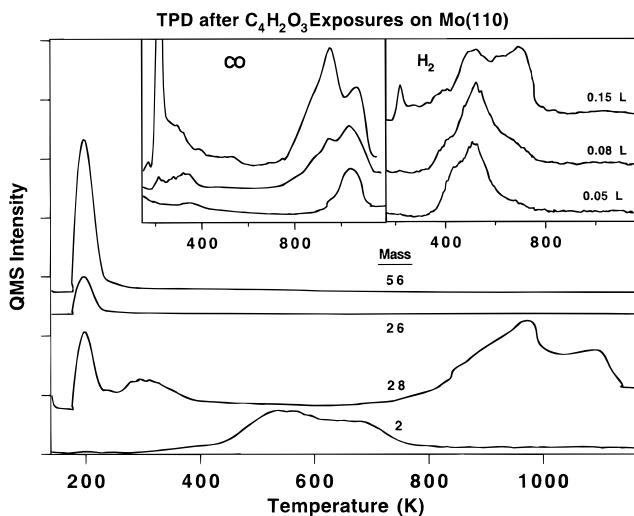
shows a sharp peak at 200 K with a shoulder on the high temperature side, a broad peak between 270 and 360 K, and two prominent peaks above 750 K. These latter two peaks are characteristic of CO formed via the recombination of adsorbed carbon ( $\text{C}_{\text{ads}}$ ) and oxygen ( $\text{O}_{\text{ads}}$ ). The features at temperatures  $<270$  K are due to cracking fragments of molecular maleic anhydride in the QMS. The peak centered at 310 K corresponds to the desorption of molecular CO formed from maleic anhydride dissociation on the surface. The assignment of this peak to CO desorption, rather than  $\text{C}_2\text{D}_2$ , is supported by the TPD spectra of the nondeuterated maleic anhydride, shown in Figure 4. As noted in Figure 4, no mass 26 desorption feature is apparent above 250 K. The inset of Figure 4 shows two series of TPD spectra monitoring CO and  $\text{H}_2$

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**Figure 3.** TPD spectra of  $D_2$ ,  $CO$ ,  $CO_2$ , and maleic anhydride desorption after dosing deuterated maleic anhydride at 100 K on the  $Pd(111)/Mo(110)$  surface.



**Figure 4.** TPD spectra of  $H_2$ ,  $CO$ ,  $CO_2$ , and maleic anhydride desorption after dosing nondeuterated maleic anhydride at 100 K on the  $Mo(110)$  surface. In the inset, TPD spectra of  $H_2$  and  $CO$  with increasing maleic anhydride exposures are shown.

desorption with increasing maleic anhydride coverages on the  $Mo(110)$  surface. From this inset it is apparent that the  $CO$  desorption feature at 310 K extends to 600 K with higher maleic anhydride coverages while the  $H_2$  desorption feature at 700 K is only observed at the higher maleic anhydride exposures. Since  $CO$  desorbs either at  $\sim 300$  K due to molecular desorption or at a temperatures higher than 750 K due to the recombination of adsorbed carbon and oxygen atoms, the  $CO$  desorption near 550 K is likely due to a reaction-limited surface process in which  $CO$  is formed and immediately desorbed.

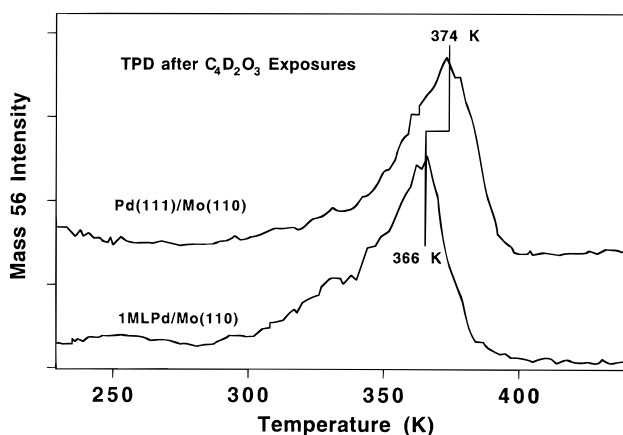
TPD spectra monitoring masses 44 and 56, corresponding to the desorption of  $CO_2$  and molecular maleic anhydride, respectively, show only a single peak at 200 K with a shoulder on the high-temperature side. Since this feature does not saturate with increasing maleic anhydride exposure, it is assigned to correspond to the desorption of multilayer maleic anhydride. The shoulder on the high temperature side is likely due to the desorption

of maleic anhydride in the second adsorption layer. The absence of any higher temperature desorption features is consistent with the complete decomposition of maleic anhydride in the first monolayer.

The adsorption and reactivity of maleic anhydride on  $Pd_{1ML}/Mo(110)$  has been also studied with TPD. The experiments carried out on the "as deposited"  $Pd_{1ML}/Mo(110)$  surface at 300 K show behavior identical to that observed for this surface annealed to 1200 K. That these two are identical is consistent with the fact that no significant alloying occurs for the  $Pd_{1ML}/Mo(110)$  system even at 1200 K. The TPD spectra monitoring masses 4, 28, 44, and 56 following various exposures of deuterated maleic anhydride are displayed in Figure 2. As seen in Figure 2, most of the maleic anhydride desorbs molecularly. The TPD spectra of the parent peak (mass 56) show a doublet at 200 and 220 K, and a third peak at 365 K, with a shoulder that extends toward lower temperature. The feature at 365 K is due to molecular desorption from the first monolayer. The peak at 200 K does not saturate with maleic anhydride exposure and shifts toward higher desorption temperatures with increasing exposures, behavior characteristic of a condensed multilayer. The feature at 220 K shows a slightly higher desorption temperature than the multilayer peak but is at a significantly lower temperature than the feature at 365 K corresponding to the chemisorbed layer. This feature likely is due to desorption from the second layer. Mass 4 ( $D_2$ ) desorption shows a very broad peak between 420 and 700 K, while the TPD spectra of mass 44 indicates a doublet at 205 K and a feature at 365 K. Since these features at mass 44 track those found for mass 56, they are assigned to correspond to the fragmentation of molecular maleic anhydride in the QMS. In addition to the above products, mass 44 also shows a broad feature between 400 and 700 K. This feature is very likely due to the desorption of  $CO_2$  formed from maleic anhydride decomposition in a reaction-limited step.

The adsorption/desorption behavior of maleic anhydride from the  $Pd(111)/Mo(110)$  surface is, in many respects, similar to that found for the  $Pd_{1ML}/Mo(110)$  surface. It is apparent from Figure 3, for example, that the major desorption product following maleic anhydride adsorption is the parent molecule. However, significant differences are clearly seen between the monolayer and multilayer  $Pd$  systems. First,  $D_2$  desorbs at 450 K from a much narrower peak on the  $Pd(111)/Mo(110)$  surface, in contrast to the very broad  $D_2$  desorption peak found for the  $Pd_{1ML}/Mo(110)$  surface. Secondly, the mass 28 TPD shows a higher temperature desorption feature at 440 K for the  $Pd(111)/Mo(110)$  surface. Finally, the mass 44 ( $CO_2$ ) TPD trace shows no desorption features above 400 K. It is noteworthy that the mass 44 TPD trace shows a much larger desorption peak at 375 K on the  $Pd(111)/Mo(110)$  surface than the corresponding peak at 365 K on the  $Pd_{1ML}/Mo(110)$  surface. Furthermore, the ratio of the peak area of the feature at 375 K relative to the feature at 200 K for mass 44 is significantly larger than the corresponding ratio for mass 56. This dissimilarity indicates that the peak at 375 K cannot be attributed solely to the fragmentation of molecular maleic anhydride in the QMS. A significant portion must be due to the desorption of  $CO_2$  formed from maleic anhydride decomposition or via a desorption-mediated dissociation process that occurs within this temperature range.

In Figure 5, the TPD spectra of the parent molecule (mass 56) on  $Pd(111)/Mo(110)$  are compared with the corresponding spectra on the  $Pd_{1ML}/Mo(110)$  surface. This comparison shows that maleic anhydride desorbs at a slightly higher temperature from the  $Pd(111)/Mo(110)$



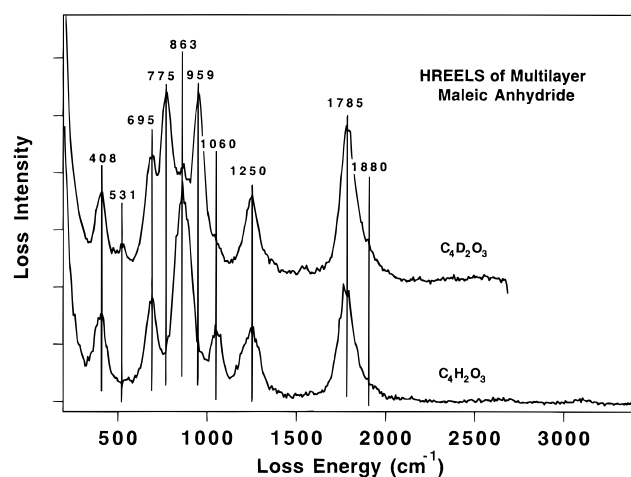
**Figure 5.** Comparison of TPD spectra of chemisorbed maleic anhydride on the Pd<sub>IML</sub>/Mo(110) surface with the Pd(111)/Mo(110) surface.

surface than from the Pd<sub>IML</sub>/Mo(110) surface. This difference, although slight, was very reproducible. This result indicates a small destabilization of the bonding of maleic anhydride on the Pd<sub>IML</sub>/Mo(110) surface relative to the Pd(111)/Mo(110) surface.

Assuming a comparable coverage of maleic anhydride within the first chemisorbed layer on Mo(110), Pd<sub>IML</sub>/Mo(110), and Pd(111)/Mo(110), the fraction of maleic anhydride that undergoes decomposition on the monolayer and multilayer palladium surfaces can be estimated from the D<sub>2</sub> TPD areas. These areas suggest this fraction to be approximately 0.15 for the Pd(111)/Mo(110) surface and 0.2 for the Pd<sub>IML</sub>/Mo(110) surface.

**3.2. High-Resolution Electron Energy Loss Spectroscopy (HREELS).** The adsorption of maleic anhydride and its deuterated counterpart on Mo(110), Pd<sub>IML</sub>/Mo(110), and Pd(111)/Mo(110) has also been studied with HREELS. Since the present study is the first HREELS investigation of maleic anhydride adsorption, we focus first on the HREELS spectrum of multilayer maleic anhydride, particularly with respect to the published infrared (IR) data of this compound. Mirone and Chiorboli<sup>22</sup> have studied solid, liquid, and gaseous maleic anhydride with IR and Raman spectroscopy. The spectral bands have been assigned on the basis of the depolarization ratios and the gas-phase band contours. Lauro et al.<sup>23</sup> have studied oriented polycrystalline maleic anhydride, both nondeuterated and deuterated, using IR spectroscopy. These authors reassigned the IR bands of Mirone and Chiorboli<sup>22</sup> on the basis of the dichroism of the crystalline spectra in polarized light and using a normal-coordinate analysis. The results of the present study are in good agreement with the results by Lauro et al.,<sup>23</sup> and thus our assignments will follow largely the assignments of these authors.

Figure 6 shows a comparison of the HREELS spectra of multilayer, nondeuterated and deuterated maleic anhydride. The HREELS spectrum of nondeuterated maleic anhydride shows features at 408, 695, 863, 1060, 1250, and 1785 cm<sup>-1</sup>, while the deuterated maleic anhydride spectrum has features at 408, 531, 695, 775, 863, 959, 1060, 1250, and 1785 cm<sup>-1</sup>. In each case, a shoulder at 1880 cm<sup>-1</sup> is clearly visible. The features at 1785 and 1880 cm<sup>-1</sup> can be assigned unambiguously to the asymmetric and symmetric C=O stretching modes. The peak at 1250 cm<sup>-1</sup>, which is unaffected by deuteration, can be assigned to the symmetric C–O stretching mode; this



**Figure 6.** The HREELS spectra of multilayer deuterated and nondeuterated maleic anhydride.

frequency is very characteristic of cyclic anhydrides. The feature at 1060 cm<sup>-1</sup> for the nondeuterated case consists of two components: a C–H bending (scissor) mode and a ring-bending (in-plane) mode with major C–C and C–O stretching components (~30% C–C and ~20% C–O).<sup>23</sup> Upon deuteration, the C–H bending mode shifts to 775 cm<sup>-1</sup>, whereas the ring-bending feature at 1060 cm<sup>-1</sup> shifts to 959 cm<sup>-1</sup>. It is noteworthy that the band at 959 cm<sup>-1</sup> for the deuterated molecule has primarily C–O stretching vibrational character (~60%). The peak at 863 cm<sup>-1</sup> can be assigned to a C–H bending (wagging) component, which shifts to 775 cm<sup>-1</sup> upon deuteration, and a C–C stretching component. The relative small shift of the wagging mode upon deuteration indicates strong coupling of this mode with other C–C or C–O modes in this energy range. The peak at 695 and 408 cm<sup>-1</sup> for both deuterated and nondeuterated maleic anhydride can be correlated with an in-plane, ring-bending mode and an in-plane C=O bending mode, respectively. The HREELS spectrum of deuterated maleic anhydride also has a peak at 531 cm<sup>-1</sup>, which is likely due to a C–D bending (twisting) mode. The assignments of the major features observed for multilayer adsorption are summarized in Table 1. For comparison, the data and assignments of Mirone and Chiorboli<sup>22</sup> and Lauro et al.<sup>23</sup> are also summarized.

**3.2.1. Maleic Anhydride on Mo(110).** Figure 7 shows a series of HREELS spectra acquired following increasing exposures of maleic anhydride to the Mo(110) surface. At the lowest coverages, four relatively weak and broad features at 350, 545, 810, and 1120 cm<sup>-1</sup> are observed. With increasing maleic anhydride exposure, these features all become more intense with the peak at 545 cm<sup>-1</sup> shifting gradually to 600 cm<sup>-1</sup>. In addition, features at 1450, 1900, and 3020 cm<sup>-1</sup> begin to develop. At the highest coverages, the feature at 1900 cm<sup>-1</sup> shifts toward lower frequency, finally residing at 1800 cm<sup>-1</sup> for multilayer maleic anhydride. Concomitantly, a peak at 1090 cm<sup>-1</sup> emerges and the peak at 1450 cm<sup>-1</sup> shifts to 1505 cm<sup>-1</sup>. A small feature at 2320 cm<sup>-1</sup> is also apparent and likely is due to adsorbed CO<sub>2</sub> formed from maleic anhydride decomposition.

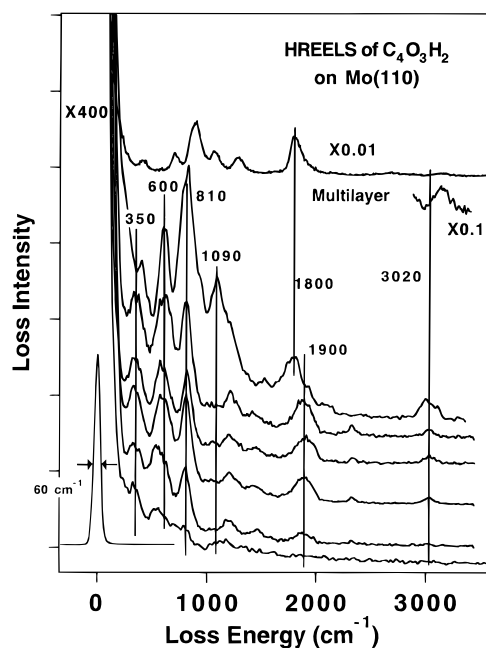
Figure 8 shows a series of HREELS spectra acquired following sequential anneals after exposure of the Mo(110) surface to 0.05 L maleic anhydride at 100 K; this exposure corresponds approximately to 60% of the saturation coverage. At 100 K, features at 350, 590, 810, 1210, 1450, 1900, 2320, and 3020 cm<sup>-1</sup> are observed. The peak at 2320 cm<sup>-1</sup> is due to the asymmetric stretching mode of physisorbed CO<sub>2</sub>, a likely product of maleic anhydride

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**Table 1. Assignment of the Vibrational Features of Multilayer Maleic Anhydride**

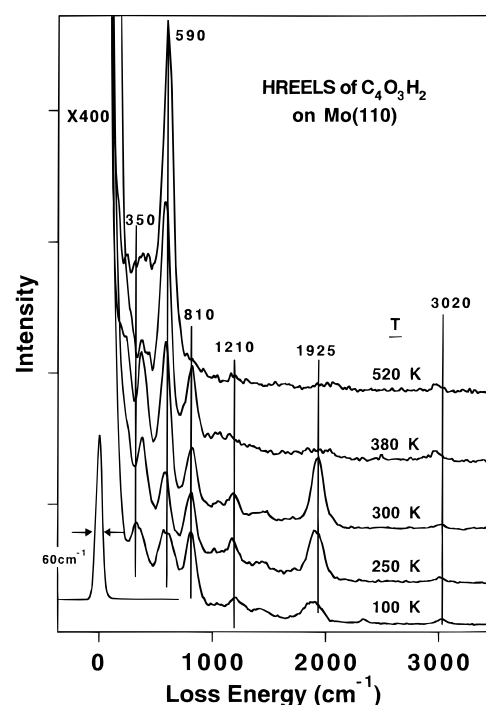
multilayer, this work	multilayer (D), this work	crystalline, Lauro et al.	crystalline (D), Lauro et al.	film, Mirone et al.	mode assignment
408	408	415	415	408	C=O bend
	531	644	532		C-H bend ?
695	695	697	685	699	ring bend
863	775	840	773	844	C-H bend
863	863	872	859	871	C-C stretch
1060	775	1061	768	1068	C-H bend
1060	959	1069	958	1057	ring bend, C-O stretch
1250	1250	1243	1238	1268	C-O stretch
1785	1785	1785	1778	1783	C=O stretch
1880	1880	1857	1842	1858	C=O stretch

**Figure 7.** HREELS spectra of maleic anhydride on the Mo(110) surface with increasing exposures.

decomposition. This assignment is consistent with the fact that this peak disappears upon heating the sample to 250 K.

From 100 to 300 K, the main changes occur at the features located at 350 and 1900  $\text{cm}^{-1}$ , which shift to higher frequency and increase in intensity. Additionally, the peak at 1450  $\text{cm}^{-1}$  shifts to 1490  $\text{cm}^{-1}$ . Upon further heating to 380 K, the peaks at 1210, 1490, and 1925  $\text{cm}^{-1}$  disappear and the feature at 380  $\text{cm}^{-1}$  attenuates. These changes correlate with the desorption of CO in the parallel TPD experiments; CO is the only desorption product in this temperature range.

The adsorption of CO on Mo(110) and oxygen-covered Mo(110) has been studied by Yates and co-workers using HREELS.<sup>24</sup> Depending on the CO coverage, the oxygen coverage, and the annealing temperature, peaks associated with the C=O moiety have been observed at 1130, 1345, 1490–1535, and 1935–2010  $\text{cm}^{-1}$ . The peak at 1130  $\text{cm}^{-1}$  has been assigned to CO lying parallel to the surface and bonded to two Mo atoms. This "lying-down" CO is suggested to be a precursor to the dissociation of CO. The peaks between 1300 and 1600  $\text{cm}^{-1}$  are consistent with CO adsorbed in a tilted configuration, from which the CO can either convert to the dissociation precursor or simply desorb, depending upon the coverage of CO and oxygen. The peak above 1900  $\text{cm}^{-1}$  is consistent with CO in a configurational perpendicular to the Mo(110) surface. Accordingly, we assign the peaks at 1925  $\text{cm}^{-1}$  to the

**Figure 8.** Annealing series of HREELS spectra after dosing submonolayer maleic anhydride on the Mo(110) surface.

stretching mode of molecularly adsorbed CO formed from maleic anhydride decomposition. Likewise, the peak at 380  $\text{cm}^{-1}$ , in turn, corresponds to the Mo–CO stretching mode. The gradual increase in intensity of the features at 380 and 1925  $\text{cm}^{-1}$  indicates the gradual formation of molecularly adsorbed CO from the decomposition of maleic anhydride. Upon heating from 300 to 380 K, some of the CO desorbs (and is detected in the TPD experiments) while a portion dissociates to  $\text{C}_{\text{ads}}$  and  $\text{O}_{\text{ads}}$ . Figure 8 also shows that the feature at 810  $\text{cm}^{-1}$  disappears after heating to 520 K. During the annealing sequence from 100 to 520 K, the feature at 590  $\text{cm}^{-1}$  steadily gains intensity; a subsequent anneal to 1200 K leads to its disappearance. Since this feature corresponds to the Mo–O stretching mode of  $\text{O}_{\text{ads}}$ ,<sup>28</sup> this HREELS result is consistent with the AES data which show that carbon is the only species left on the surface after heating to 1200 K. It should also be noted that the feature related to the C–H stretching mode shifts from 3020 to 2970  $\text{cm}^{-1}$  with annealing from 300 to 380 K, suggesting further rehybridization of the olefin carbons of maleic anhydride from  $\text{sp}^2$  toward  $\text{sp}^3$ .

The thermal behavior of a saturated monolayer of maleic anhydride was also studied with HREELS. In Figure 9,

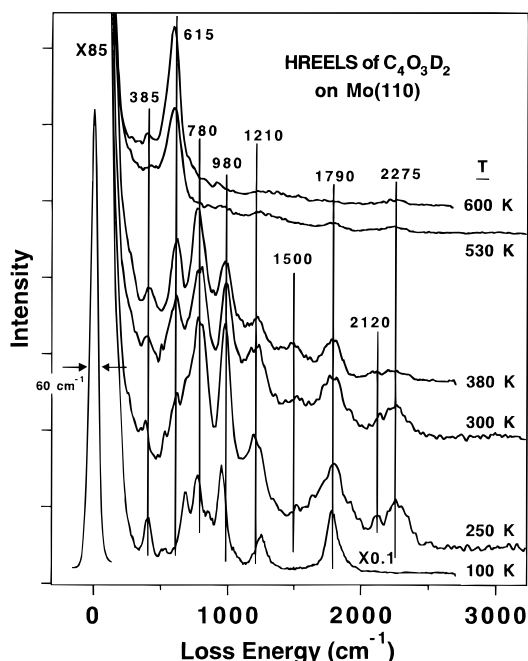
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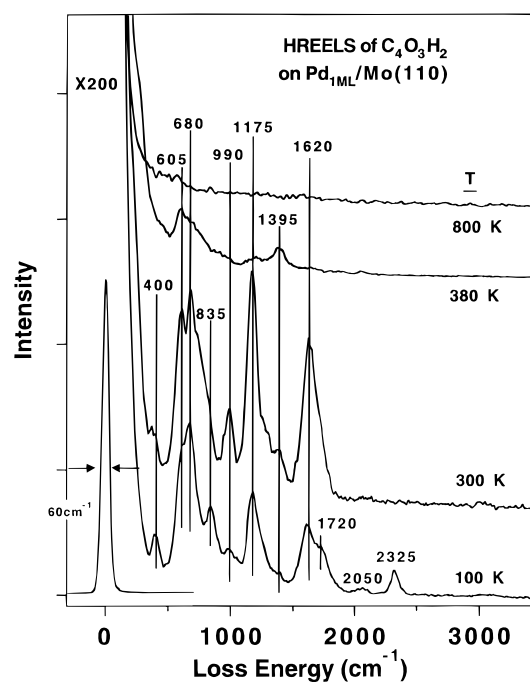


**Figure 9.** Annealing series of HREELS spectra after dosing 5 ML deuterated maleic anhydride on the Mo(110) surface.

HREELS spectra are shown that were acquired after exposure of the Mo(110) surface at 100 K to approximately five monolayers of deuterated maleic anhydride and then subsequently heated to the indicated temperature. Higher coverages of maleic anhydride show a similar annealing behavior; however, the features associated with the carbonyl group frequencies disappear at a higher annealing temperature. This result is consistent with the TPD results, which show that CO desorbs up to 600 K at the higher maleic anhydride coverages. It is also noteworthy that the carbonyl stretching mode at 1790  $\text{cm}^{-1}$ , a value similar to that for the condensed layer, but significantly lower than that found for the lower maleic anhydride coverages. This feature does not shift to higher frequency, but simply gradually loses intensity. This same behavior has been observed for both nondeuterated (not shown) and deuterated maleic anhydride at saturation coverage. This suggests that no molecularly adsorbed CO is present on the surface and that the decomposition of maleic anhydride occurs at a higher temperature for the higher coverages compared to the lower coverages.

An HREELS spectrum of the first adsorbed layer of deuterated maleic anhydride (spectrum taken after heating to 250 K) reveals features at 385, 615, 780, 980, 1210, 1790, 2120, and 2275  $\text{cm}^{-1}$ . Upon heating from 250 to 380 K, the peaks at 980, 1210, 1790, 2120, and 2275  $\text{cm}^{-1}$  gradually lose intensity, while the peak at 615  $\text{cm}^{-1}$  steadily gains intensity. Following an anneal to 300 K, a peak at 1500  $\text{cm}^{-1}$  is clearly visible. Further heating to 530 K leads to the disappearance of the features at 780, 980, 1220, 1500, 1790, 2120, and 2275  $\text{cm}^{-1}$ . As for the nondeuterated maleic anhydride, the feature at 615  $\text{cm}^{-1}$  is the only remaining feature following the 530 K anneal; this feature, as indicated above, corresponds to the Mo–O stretching vibration<sup>25</sup> and disappears after annealing to 1200 K.

A comparison of the HREELS spectra of nondeuterated maleic anhydride with the spectra of deuterated maleic anhydride suggests that the peak near 800  $\text{cm}^{-1}$  corresponds to a C–C stretching mode. The peak at 1080  $\text{cm}^{-1}$ , which shifts to 980  $\text{cm}^{-1}$  upon deuteration, can be assigned to a ring-bending mode. The peaks at 1220 and 1500  $\text{cm}^{-1}$

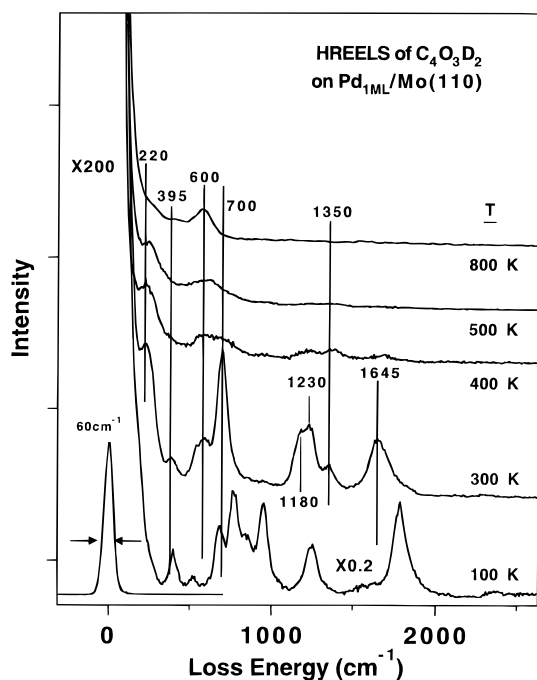


**Figure 10.** HREELS spectra of maleic anhydride on the Pd<sub>1ML</sub>/Mo(110) surface after dosing at 100 K and subsequent annealing to the indicated temperature.

can be assigned to the symmetric C–O–C (or simply C–O) and C=C stretching vibration, respectively. The assignment of the feature at 2120  $\text{cm}^{-1}$  is believed to be a combination mode, possible involving the C=O stretching and bending modes in Fermi resonance with the C–D stretching vibration.

**3.2.2. Maleic Anhydride on Pd<sub>1ML</sub>/Mo(110) and Pd(111)/Mo(110).** In Figure 10, HREELS spectra are shown of maleic anhydride on Pd<sub>1ML</sub>/Mo(110) taken subsequent to dosing monolayer maleic anhydride at 100 K and then annealing to the indicated temperature. At 100 K, features at 400, 605, 680, 835, 990, 1175, 1395, 1620, 1720, 2050, and 2325  $\text{cm}^{-1}$  are apparent. Upon annealing to 300 K, the features at 835, 1720, 2050, and 2325  $\text{cm}^{-1}$  disappear, while the remaining features, with the exception of the peak at 400  $\text{cm}^{-1}$ , grow in intensity. It should be noted also that two shoulders at 800 and 1300  $\text{cm}^{-1}$  are now clearly visible as well. The features at 2050 and 2325  $\text{cm}^{-1}$  can be attributed to the C=O stretching mode of molecularly adsorbed CO and to the asymmetric CO<sub>2</sub> stretching mode of molecularly adsorbed CO<sub>2</sub>. Both are likely products of maleic anhydride decomposition, and both desorb upon heating to 300 K. These results are consistent with the fact that CO<sub>2</sub> only physisorbs on the Pd(111) surface and that CO has a significantly reduced binding energy on the monolayer palladium surface. The peaks at 835 and 1720  $\text{cm}^{-1}$  are likely due to weakly adsorbed maleic anhydride either in the first or second layer. Further annealing to 380 K leads to the disappearance or marked attenuation of the features at 400, 605, 680, 800, 980, 1175, 1300, and 1720  $\text{cm}^{-1}$ , consistent with the desorption of maleic anhydride in parallel TPD experiments.

Figure 11 shows a series of HREELS spectra acquired subsequent to dosing approximately five monolayers of deuterated maleic anhydride to the Pd<sub>1ML</sub>/Mo(110) surface at 100 K and annealing to the indicated temperature. After heating to 300 K, features at 220, 395, 600, 700, 1200, 1350, and 1645  $\text{cm}^{-1}$  are observed. The peak near 1200  $\text{cm}^{-1}$  is unusually broad and consists of two components, one at 1180 and a second at 1230  $\text{cm}^{-1}$ . Further

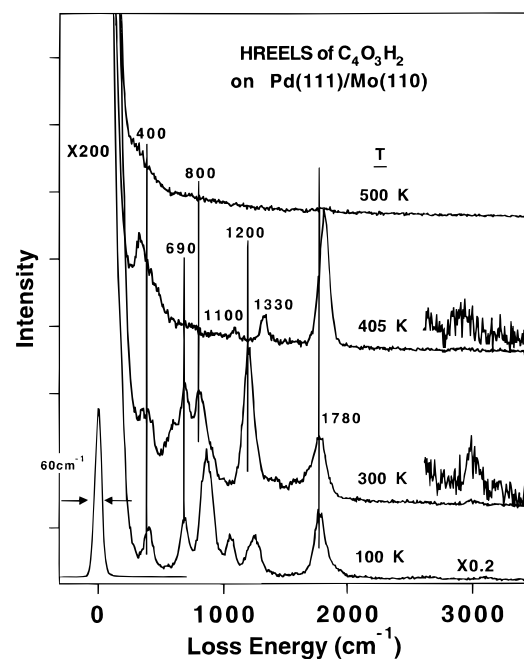


**Figure 11.** HREELS spectra of deuterated maleic anhydride on the Pd<sub>1ML</sub>/Mo(110) surface after dosing at 100 K and subsequent annealing to the indicated temperature.

annealing to 400 K leads to the disappearance of the features related to molecular maleic anhydride, leaving features at 220, 700, 1210, and 1470 cm<sup>-1</sup>. The feature at 600 cm<sup>-1</sup> does not disappear even after heating to 800 K and likely is due to the presence of trace oxygen on the surface or in the subsurface region.

Comparing the spectra of the deuterated and nondeuterated maleic anhydride as a function of the anneal temperature, it is clear that both molecular and dissociative maleic anhydride are present on the surface between 250 and 500 K. Molecular maleic anhydride dominates the spectra at 300 K, and subsequently desorbs at 366 K. The features at 400 (395), 680 (700), 835, 1175 (1180), 1300 (1230), and 1610 (1650) correspond to the molecular species. The presence of an intense C–O–C symmetric vibration at 1175 (1180) and a ring-bending mode at 680 (700) cm<sup>-1</sup> is consistent with the TPD results indicating that the maleic anhydride adsorbs molecularly. However, the large red-shift of the C=O stretching mode suggests a significant interaction between the carbonyl group and the surface. This, coupled with the indicated interaction of the molecule with the surface through the olefin bond, indicates a flat “lying-down” configuration. Consistent with this bonding picture, a feature at 1300 cm<sup>-1</sup>, which shifts only slightly to 1230 cm<sup>-1</sup> upon deuteration, can be assigned to the C=C stretching mode of maleic anhydride. The relatively high frequency of this peak indicates that the C=C double bond is largely retained upon adsorption. However, the large shift from 1595 cm<sup>-1</sup> for maleic anhydride in the condensed layer to 1230 cm<sup>-1</sup> observed on the Mo(110) surface indicates a strong interaction between the surface and the C=C double bond. Therefore, maleic anhydride is bonded to the surface via the olefin  $\pi$ -bond with the molecular plane parallel to the surface (see also below). As a consequence, the two carbonyl groups of the molecule interact with the surface, leading to a red-shift of their vibrational frequencies.

After desorbing the molecular maleic anhydride by heating to 380 K, no carbonyl-related feature is observed. The molecular dissociation apparently takes place well below 300 K, as evidenced by the appearance of the feature



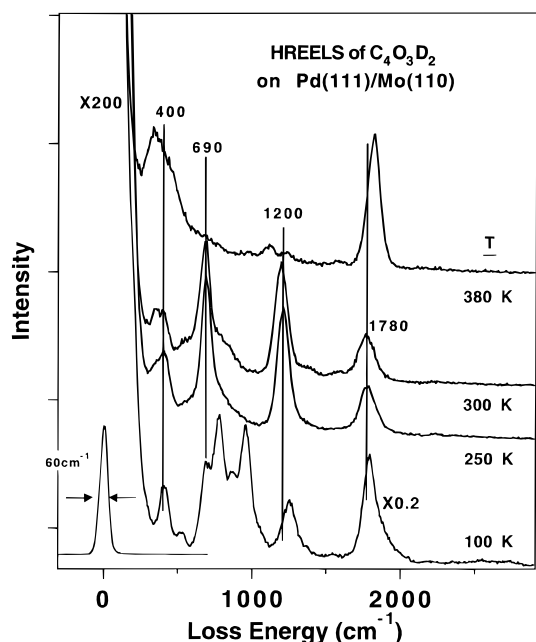
**Figure 12.** HREELS spectra of maleic anhydride on the Pd(111)/Mo(110) surface after dosing at 100 K and subsequent annealing to the indicated temperature.

at 1395 (1350) cm<sup>-1</sup> at the lower temperatures. The dissociation products, CO and CO<sub>2</sub>, desorb well below 380 K; thus the C=O stretching feature is not observed in the spectrum at 380 K. The products of the dissociation which remain on the surface after annealing to 380 K likely are species containing C=C or C=C–C units. The feature at 1395 cm<sup>-1</sup> shifts only slightly to 1350 cm<sup>-1</sup> upon deuteration, and thus is assigned to the C=C stretching mode. The feature at 980 cm<sup>-1</sup>, which is not seen in the spectrum of deuterated maleic anhydride, can be assigned to the symmetric C–H deformation. This result indicates that the dissociation product, likely acetylene, is also bonded to the surface in a  $\pi$ -bond configuration.

HREELS spectra acquired following the adsorption of maleic anhydride onto a Pd(111)/Mo(110) surface are shown in Figures 12 and 13. The spectra of Figure 12 were acquired after dosing maleic anhydride onto a 100 K Pd(111)/Mo(110) substrate and then annealing to the indicated temperature. For reference, the spectrum of multilayer maleic anhydride is shown at the bottom of Figure 12. The spectrum after annealing the sample to 300 K shows features at 400, 600, 690, 800, 1200, 1780, and 2995 cm<sup>-1</sup>. Following an anneal to 405 K, the features at 400, 600, 690, 800, 1200, 1780, and 2995 cm<sup>-1</sup> disappear and new features at 330, 1100, 1330, and 1810 cm<sup>-1</sup> are apparent. The feature at 330 cm<sup>-1</sup> has a shoulder at 450 cm<sup>-1</sup> which can be resolved from the primary 320 cm<sup>-1</sup> peak by acquiring the spectrum in an off-specular geometry. Upon further annealing to 500 K, no features are observed (upper HREELS spectrum).

Figure 13 shows a series of HREELS spectra acquired following the dosing of deuterated maleic anhydride to a Pd(111)/Mo(110) surface and then annealing to the indicated temperatures. The spectrum taken after heating to 250 K displays features at 400, 540, 690, 1200, and 1780 cm<sup>-1</sup>. With further annealing to 300 K, little change is apparent except for a new feature at 340 cm<sup>-1</sup>. The spectrum taken after annealing to 380 K shows features at 320, 430, 990, 1105, 1225, and 1810 cm<sup>-1</sup>.

Similar to the behavior observed for the Pd<sub>1ML</sub>/Mo(110) surface, both molecularly and dissociatively adsorbed maleic anhydride are seen. The molecularly adsorbed



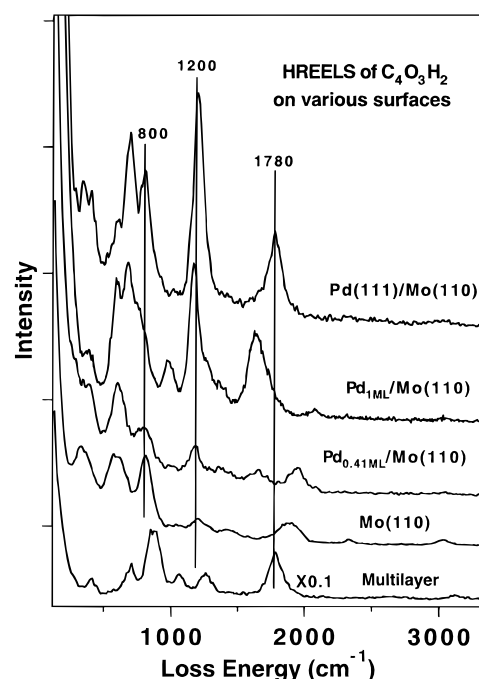
**Figure 13.** HREELS spectra of deuterated maleic anhydride on the Pd(111)/Mo(110) surface after dosing at 100 K and subsequent annealing to the indicated temperature.

**Table 2. Vibrational Frequencies of Chemisorbed Maleic Anhydride and Deuterated Maleic Anhydride on the Pd<sub>1ML</sub>/Mo(110) and Pd(111)/Mo(110) Surfaces**

Pd <sub>1ML</sub> /Mo(110)		Pd(111)/Mo(110)		mode assignment
C <sub>4</sub> O <sub>3</sub> H <sub>2</sub>	C <sub>4</sub> O <sub>3</sub> D <sub>2</sub>	C <sub>4</sub> O <sub>3</sub> H <sub>2</sub>	C <sub>4</sub> O <sub>3</sub> D <sub>2</sub>	
400	395	400	400	C=O bending
680	700	690	690	ring bending
990	700			C-H bending
		800	(540?)	C-H deformation
1175	1180	1200	1200	C-O-C
1300	1230			C=C
1620	1645	1780	1780	C=O

maleic anhydride disappears after annealing to 405 K, consistent with a desorption temperature of 374 K found in the parallel TPD measurements. The features at 400 (400), 690 (690), 800 (540), 1200 (1200), and 1780 (1780) cm<sup>-1</sup> can be assigned to the C=O bending mode, the ring-bending mode, the C-H deformation mode, the C-O-C symmetric stretching modes, and the C=O stretching modes, respectively. It is noteworthy that the C=O carbonyl stretching mode shows the same frequency as that for the condensed layer. The absence of any shift indicates that there is no significant interaction between the C=O double bond and the surface and that molecularly adsorbed maleic anhydride is bonded to the surface in a di-σ-configuration. Consistent with this is the observation that no peak related to the C=C stretching vibration is apparent. The observed vibration frequencies for the maleic anhydride and nondeuterated maleic anhydride on the Pd<sub>1ML</sub>/Mo(110) and Pd(111)/Mo(110) surfaces are summarized in Table 2.

The frequency of the C-H (C-D) stretching mode has been shown to correlate well with the hybridization of the carbon atom, therefore the frequency of this vibration on the Pd<sub>1ML</sub>/Mo(110) surface is compared with the corresponding mode on the Pd(111)/Mo(110) surface in Table 3. These data are from spectra taken at 15° off-specular, where the C-H (C-D) can be observed with high intensity. The results of Table 3 indicate that the Pd(111)/Mo(110) surface exhibits a higher C-H (C-D) vibrational frequency than the corresponding frequency on the Pd<sub>1ML</sub>/Mo(110) surface. These results indicate that the olefine



**Figure 14.** Comparison of maleic anhydride HREELS spectra on various surfaces.

**Table 3. C-H (C-D) Stretching Vibration Frequencies of Maleic Anhydride**

	nondeuterated maleic anhydride	deuterated maleic anhydride
Pd <sub>1ML</sub> /Mo(110)	3045	2300
Pd(111)/Mo(110)	2995	2230
Mo(110)	3020	2275

double bond in maleic anhydride is rehybridized significantly more from the sp<sup>2</sup> configuration toward the sp<sup>3</sup> configuration on the Pd(111)/Mo(110) surface compared to the Pd<sub>1ML</sub>/Mo(110) surface.

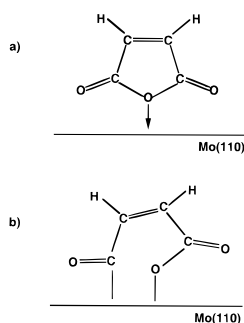
The peaks at 320 (320) and 1810 (1810) cm<sup>-1</sup> are due to the Pd-CO and C-O stretching vibrations of molecularly adsorbed CO formed from maleic anhydride dissociation. Figures 12 and 13 indicate that CO forms upon annealing to 405 K, desorbing with further heating to 500 K. Previous HREELS studies of Gates and Kesmodel<sup>26-29</sup> on the adsorption of ethylene and acetylene on Pd(111) indicate that the features at 450 (430), 1100 (1105), and 1320 (990) can be assigned to the Me-C, C-C stretching, and CH<sub>3</sub> deformation of an ethylidyne species.

**3.2.3. Comparison of HREELS Spectra on Various Surfaces.** Figure 14 compares the HREELS spectra for maleic anhydride adsorbed on Mo(110), Pd<sub>0.4ML</sub>/Mo(110), Pd<sub>1ML</sub>/Mo(110), and Pd(111)/Mo(110) surfaces. The multilayer maleic anhydride spectrum is also included for reference. As pointed out previously, the C=O stretching vibration is red-shifted on Mo(110), blue-shifted on Pd<sub>1ML</sub>/Mo(110), and unshifted on Pd(111)/Mo(110). Also seen is the dramatic intensity increase of the O-C-O stretching vibrational mode near 1200 cm<sup>-1</sup>. The C-C stretching mode at 800 cm<sup>-1</sup> shows a high intensity on the Mo(110) surface. The intensity of this mode decreases with increasing Pd coverage and disappears on the Pd(111)/Mo(110) surface; for this latter surface the C-H bending mode appears.

## 4. Discussion

**4.1. Maleic Anhydride Adsorption on Mo(110).** In the first chemisorbed layer on Mo(110), maleic anhydride





**Figure 15.** Proposed adsorption geometry of maleic anhydride on the Mo(110) surface.

decomposes completely to form CO, H<sub>2</sub>, and adsorbed carbon upon heating. The highly reactive nature of the Mo(110) surface toward maleic anhydride is not unexpected when considering previous studies on this surface. For example, the adsorption of C<sub>2</sub>H<sub>4</sub> on Mo(110) has been studied by Young and Slavin<sup>30</sup> who found that ethylene completely decomposed to form hydrogen and carbon with no molecular desorption. Serafin and Friend<sup>31</sup> found that approximately 70% of adsorbed pyridine on Mo(110) decomposed to form C<sub>ads</sub>, N<sub>ads</sub>, and gas-phase H<sub>2</sub>. The high affinity of Mo toward the formation of an oxide serves as a strong driving force for the decomposition of oxygen-containing compounds such as maleic anhydride. The work here suggests that even below 300 K bond-breaking processes have already begun for low coverages of maleic anhydride. This is clearly evident in Figure 8, where molecularly adsorbed CO has already formed subsequent to annealing to 250 K; the evidence is the simultaneous growth of the features at 380 and 1925 cm<sup>-1</sup>. However, at relatively high maleic anhydride coverages, the surface reactivity is inhibited due to self-poisoning. Under these conditions, no molecular CO is observed on the surface following an anneal since the dissociation of maleic anhydride now occurs at a comparable temperature as that for CO desorption or dissociation. That is, the CO product either desorbs or dissociates. Furthermore, in contrast to the 150 cm<sup>-1</sup> red-shift of the carbonyl group frequency observed for the relative low coverages of maleic anhydride at 100 K, no such shift is seen for the saturated maleic anhydride coverage. This is consistent with a reduced interaction between the Mo(110) surface and maleic anhydride with increasing coverage.

The adsorption geometry of maleic anhydride apparently changes with increasing coverage. At relative low maleic anhydride coverages, the molecule is adsorbed via the oxygen lone pair as shown schematically in Figure 15a. This adsorption geometry is inferred from the following observations: (1) The symmetric C–O–C stretching mode has a relatively low intensity. This vibrational mode is typical for cyclic anhydrides and is present with relatively high intensity in the HREELS spectra for the Pd<sub>1ML</sub>/Mo(110) and the Pd(111)/Mo(110) surfaces. This result indicates that bonding through the ring oxygen considerably reduces the dynamic dipole of the C–O–C vibration. (2) The C=O stretching mode of adsorbed maleic anhydride at low coverages is blue-shifted by 150 cm<sup>-1</sup> compared to the free molecule, indicating the weakening or even scission of an adjacent bond forming the species illustrated in Figure 15b. (3) The Mo–O vibrational mode is observed with relative high intensity even at 100 K. (4) The C–C single bond stretching mode exhibits a high intensity near 800 cm<sup>-1</sup>, consistent with a “standing-up” geometry. (5) The C=C stretching mode

exhibits a very high frequency (1500 cm<sup>-1</sup>), very close to that of the condensed layer, suggesting that the C=C double bond is not perturbed by the surface and that no significant interaction between the surface and olefin double bond is present. (6) The C–H stretching mode exhibits a relatively high intensity and high frequency, while the C–H out-of-plane bending mode is not observed. These results support the conclusion that the olefin carbon atoms are largely sp<sup>2</sup> hybridized and that the molecular plane is parallel to the surface normal.

At higher maleic anhydride coverages, the feature related to the ring-bending mode appears with relatively high intensity, suggesting a tilting of the molecular plane away from the surface normal. This follows from the fact that the ring-bending mode has its largest dynamic dipole oriented perpendicular to the molecular plane.

It is also noteworthy that desorption of the second layer of maleic anhydride on Mo(110) shows a lower desorption temperature relative to the Pd<sub>1ML</sub>/Mo(110) and Pd(111)/Mo(110) surfaces, presumably because of the altered adsorption geometry in the first adsorbed layer. On the Mo(110) surface, the molecular plane is oriented essentially parallel to the surface normal, while the molecular plane is tilted markedly on the Pd(111)/Mo(110) surface and essentially parallel to the surface on the Pd<sub>1ML</sub>/Mo(110) surface. The “standing-up” molecular geometry presumably exhibits a smaller van der Waals interaction with the second layer relative to the “lying-down” molecule. As a result, two well-separated peaks are observed for the multilayer and the second layer on the Pd<sub>1ML</sub>/Mo(110) and Pd(111)/Mo(110) surfaces, while only a shoulder is observed for the second layer desorption from the Mo(110) surface at a similar coverage.

**4.2. Maleic Anhydride Adsorption on Pd<sub>1ML</sub>/Mo(110) and Pd(111)/Mo(110).** The adsorption of maleic anhydride is largely reversible on both Pd<sub>1ML</sub>/Mo(110) and Pd(111)/Mo(110) surfaces, with only 15–20% of the adsorbed maleic anhydride undergoing decomposition. The Pd(111)/Mo(110) surface shows a slightly higher binding energy for the maleic anhydride than the Pd<sub>1ML</sub>/Mo(110) surface. Despite this, the Pd<sub>1ML</sub>/Mo(110) surface shows a slightly higher tendency toward maleic anhydride decomposition, suggesting a lower activation energy for molecular decomposition on the Pd<sub>1ML</sub>/Mo(110) surface. These differences in bonding energies and activation energies for decomposition originate in the modified bonding geometries in these two systems.

The HREELS results also indicate two different bonding geometries for maleic anhydride on these two surfaces. The relatively high frequency of the C=C and C–H (C–D) stretching modes and the shift of the carbonyl mode suggest a  $\pi$ -bound species on the Pd<sub>1ML</sub>/Mo(110) surface. The absence of the C=C double bond mode as well as the lack of any shift in the carbonyl mode together with the relatively low frequency of the C–H (C–D) mode indicate a di- $\sigma$  bound species on the Pd(111)/Mo(110) surface. In the  $\pi$ -bound species, the molecular plane of the maleic anhydride is oriented parallel to the surface, permitting the carbonyl group to interact strongly with the surface. On the other hand, the molecular plane is tilted away from the surface in the  $\sigma$ -bound configuration. With respect to the above considerations, it is worthwhile to review the adsorption of ethylene on Pd(111) and on a supported Pd monolayer.

The adsorption of ethylene on the Pd(111) surface has been extensively studied and found to be bonded in a  $\pi$ -bound configuration. In contrast, maleic anhydride adsorbs on the Pd(111)/Mo(110) surface in a di- $\sigma$  bound configuration. This modification of the bonding is likely due to the enhanced ability of the C=C double bond in

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maleic anhydride to accept back-donation from the d-electronic states of the surface into the  $\pi^*$  states. The presence of the carbonyl group in the maleic anhydride also enhances the bonding of the olefinic bond to the surface relative to ethylene.<sup>28</sup>

Heitzinger et al.<sup>15</sup> have studied the adsorption of ethylene on a Pd monolayer supported on Mo(100) using HREELS and TPD. By comparing their results with the results on a Pd(100) surface, they have shown that the desorption temperature of ethylene is decreased from 287 K on multilayer Pd to 247 K on monolayer Pd. Also these authors showed that ethylene is bonded in a  $\pi$ -configuration on the Pd<sub>IML</sub>/Mo(100) surface and in a di- $\sigma$  configuration on the Pd(100) surface. The changes in the adsorption geometry observed in this study are consistent with the results of Heitzinger et al.; however, the decrease in the binding energy of maleic anhydride from multilayer Pd to monolayer Pd is somewhat smaller compared to that of ethylene. This smaller change of maleic anhydride can be ascribed to the compensating bonding by the carbonyl groups in the  $\pi$ -configuration. The interaction of the carbonyl groups with the surface is also likely responsible for the slightly lower activation energy observed for maleic anhydride decomposition on the Pd<sub>IML</sub>/Mo(110) surface. Other contributing factors for the slightly lower activation energy for decomposition on the Pd<sub>IML</sub>/Mo(110) surface could be the relative differences in the binding energies of the dissociation products on Pd<sub>IML</sub>/Mo(110) and Pd(111)/Mo(110). CO as one of the primary dissociation products desorbs upon maleic anhydride decomposition on the Pd<sub>IML</sub>/Mo(110) surface. On the other hand, CO formed from maleic anhydride decomposition on Pd(111)/Mo(110) remains on the surface, inhibiting further maleic anhydride decomposition. It is noteworthy that maleic anhydride decomposition on the Pd(111)/Mo(110) surface occurs in a narrow temperature window where the CO<sub>2</sub> that forms desorbs immediately, with any CO product remaining on the surface. On the Pd<sub>IML</sub>/

Mo(110) surface, however, maleic anhydride decomposition occurs over a relatively wide temperature range as indicated by the broad desorption peak of the decomposition products CO<sub>2</sub> and H<sub>2</sub>; no significant CO desorption is observed. The different chemistry of these surfaces toward maleic anhydride decomposition most surely is related to the differences found in the molecular adsorption geometries.

## 5. Conclusions

The adsorption of maleic anhydride is irreversible on the Mo(110) surface, while only 15–20% of adsorbed maleic anhydride on Pd<sub>IML</sub>/Mo(110) and Pd(111)/Mo(110) undergoes decomposition upon heating. Due to the stability of the Mo–O bond, the maleic anhydride is adsorbed through the ring-oxygen atom with its molecular plane essentially normal to the Mo(110) surface. For the Pd<sub>IML</sub>/Mo(110) and Pd(111)/Mo(110) surfaces, the bonding of maleic anhydride is through the olefin bond, in a di- $\sigma$  bound configuration for the Pd(111)/Mo(110) surface and in a  $\pi$ -bound configuration for the Pd<sub>IML</sub>/Mo(110) surface. A strong interaction of the carbonyl groups of maleic anhydride with the Pd<sub>IML</sub>/Mo(110) surface results in a red-shift of the C=O stretching modes. This interaction also compensates for the weaker olefin bond strength to the Pd multilayer surface relative to the Pd monolayer surface, yielding similar desorption temperatures for maleic anhydride on both surfaces.

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