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UV/HREELS spectroscopy of benzene on Pt(110)

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Some years ago, LEED studies of Ogletree et al. and Wander et al. found that benzene undergoes a structural rearrangement when the benzene adsorbs on platinum. In contrast, Horsley et al. proposed that the benzene adsorbs without undergoing significant distortion. In this paper UV/HREELS spectroscopy is used to examine benzene adsorption on Pt(110). We find that the benzene can adsorb into two different states: a weakly bound form of benzene with UV/HREELS spectrum similar to gas-phase benzene, and a strongly bound form of benzene with UV/HREELS and IR/HREELS spectra which are consistent with formation of a diene (e.g., 1,4-cyclohexadiene). A comparison of our data to the results of Wander et al. and Horsley et al. shows that the weakly bound form of benzene is consistent with Horsley's assignments, while the strongly bound species looks as expected from the work of Wander et al. The conclusion from our study then is that Wander et al. and Horsley et al. are both correct. They are just studying different forms of benzene on the platinum surface.

Keywords: benzene, platinum, UV/HREELS, electron spectroscopy, electronic spectra

1. Introduction

Some years ago, Ogletree et al. [1] examined the coadsorption of benzene and CO on Pt(111) with LEED, and found that the benzene undergoes marked structural changes upon adsorption. Wander et al. [2] later showed that the distorted benzene forms even in the absence of CO. Wander et al. also proposed that at low coverages the benzene goes into a buckled configuration. Somers et al. [4] also report that the benzene is distorted.

In contrast, Horsley et al. [3] examined the same system with NEXAFS. Horsley et al. did not find any evidence for distorted benzene. Instead they said that the benzene was largely undistorted upon adsorption.

Presently, the available spectroscopy does not allow one to distinguish between these two possibilities. The available vibrational spectra [5–9] indicate a benzene structure. However, we will see later in the paper that a distorted species such as cyclohexadiene fits the vibrational data just as well as benzene. UPS data are available [4,10] but they are hard to interpret [11].

In this paper we examined the UV/HREELS spectrum of benzene adsorbed on Pt(110). UV/HREELS spectroscopy is very sensitive [12–14] to rehybridizations. If benzene distorts as proposed by Wander et al., the benzene should show large changes in the UV/HREELS spectrum. On the other hand, if Horsley et al. are correct, the UV/HREELS spectrum should look like gas-phase benzene. In this paper we took UV/HREELS spectra to see if Wander et al. or Horsley et al. are correct. We did all of our work on Pt(110). Previous workers [15–17] have found that benzene on Pt(110) looks very similar to benzene on Pt(111).

2. Experimental

The experiments reported here were done in two different UHV chambers described previously [18–21]. The chambers are of standard design, with a PhI LEED and sputter gun, and a Riber or UTI mass spectrometer. The chamber is pumped with a diffusion pump and an ion pump or a turbo pump. During an experiment the typical background pressure is about 1×10^{-10} Torr.

The UV/HREELS measurements made here were done with an LK2000 EELS spectrometer modified with computer-controlled electronics and a stabilized power supply. We used a 15 eV incident energy relative to direct reflection and measured at a resolution of 14 meV. Details of the experimental techniques will be submitted elsewhere [21]. Generally, we find that we can measure accurate UV/HREELS spectra of adsorbed molecules with a

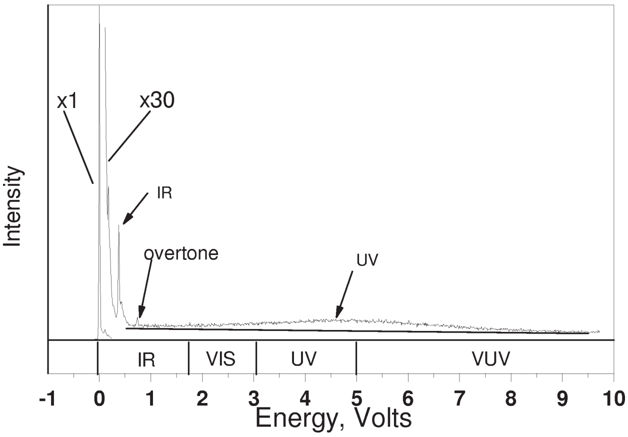

Figure 1. An EELS spectrum taken by exposing a clean, 100 K Pt(110) sample to 0.4 L of benzene and then scanning out to 10 eV.

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slightly modified EELS machine provided that we choose an incident energy below the plasmon energy of the surface, so we avoid dominating the UV/HREELS spectra by the plasmon loss.

Figure 1 shows what the raw data are like at 0.4 L exposure. Generally we scan from the infrared into the vacuum ultraviolet, that is from 0 to 10 eV. We use a 9.15 meV step size, so the spectrum takes a reasonable amount of time. The UV/HREELS peaks are generally broad and relatively weak. With benzene, the UV/HREELS features have an intensity on the order of 3% of the IR modes.

3. Results

Figure 2 shows a series of UV/HREELS spectra taken by adsorbing various amounts of benzene onto a clean 100 K Pt(110) sample and then scanning from 0.5 to 9.5 eV. At low exposures, we observe a broad peak centered at 4.9 eV. The 4.9 eV peak grows with coverage, but is relatively weak. However, as soon as the coverage is increased to 0.6 L the UV/HREELS spectrum changes markedly. There are distinct peaks at 0.75, 3.82, 4.71, 6.20, and 6.84 eV. There are also shoulders at 4.92 and 7.90 eV. The peaks grow with increasing coverage up to 1 L exposure. In other work we have found that the peaks continue to grow with additional exposure as multi-layers condense on the surface.

Figure 3 shows an expanded view of the 0.4 L exposure spectrum. Again, there is a broad peak centered at about 4.9 eV. This expanded view shows some fine structure. Interestingly, we recorded three different spectra in a row and all three spectra showed the same fine structure.

We have done several measurements to see whether the fine structure is reproducible. We found that as soon as we annealed the surface the fine structure changed. When we cleaned the surface and re-prepared the layer, we got back to almost the same fine structure. At present, we do not understand the fine structure. Still, it is clear that the 0.4 L spectrum and the other spectra taken at low coverage look markedly different from the high-coverage spectrum.

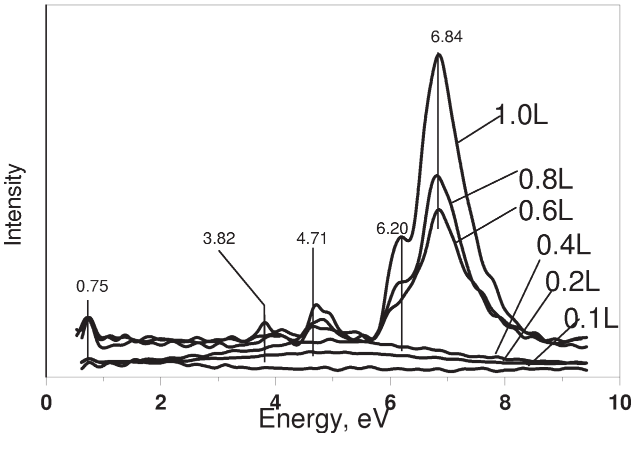

Figure 2. A series of EELS spectra taken by exposing a clean 100 K Pt(110) sample to various amounts of benzene and then scanning out to 10 eV.

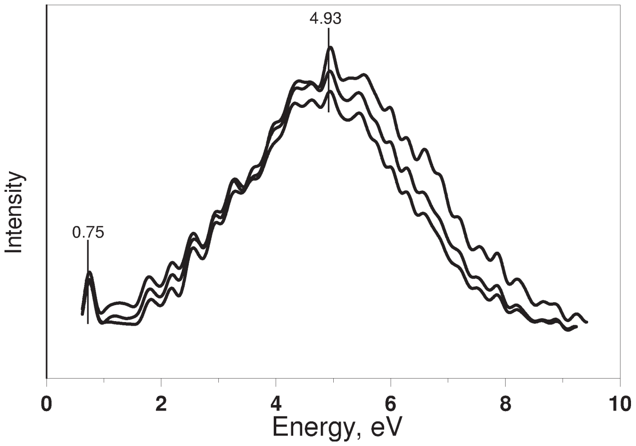

Figure 3. EELS spectra taken by exposing a clean 100 K Pt(110) sample to 0.4 L of benzene, and then recording three sequential spectra.

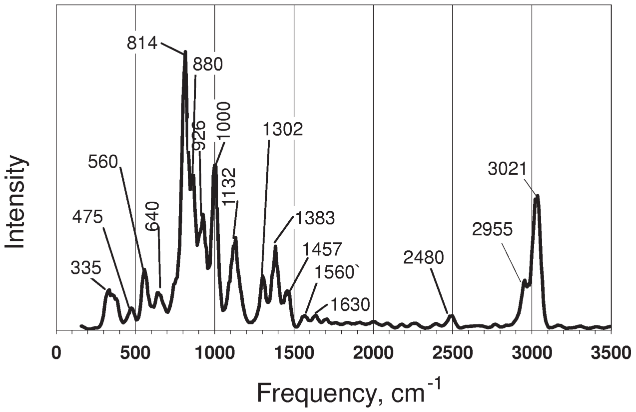

Figure 4. The vibrational plot of an EELS spectrum taken by adsorbing 0.4 L of benzene onto a clean 100 K Pt(110) sample and then scanning.

Finally, figure 4 shows a series of vibrational spectra of 0.4 L of benzene. One observes sharp peaks at 560, 640, 814, 926, 1000, 1132, 1302, 1383, 1457, 2955, and 3021 cm^{-1} and smaller features at 880, 1560, 1630, and 2480 cm^{-1}. The spectra look similar to those reported previously [7,9,17] for benzene on Pt(111) and Pt(110), except that they are at higher resolution.

We have also done TPD experiments for adsorbed benzene. Generally, we find that, at exposures up to 0.5 L, the benzene is strongly chemisorbed to the surface. This strongly bound benzene mainly decomposes, although there is some benzene desorption at about 250 and 410 K. In comparison, at higher exposures a desorption state at 180 K comes into the spectrum. Our interpretation is that the 3.82, 4.71, 6.20, and 6.84 eV states correspond to the weakly bound benzene while the broad, 4.9 eV peak corresponds to the strongly bound species.

4. Discussion

The results here show that there are two forms of benzene on Pt(110): a weakly bound form with strong UV/HREELS resonances at 3.82, 4.71, 6.20, and 6.84 eV and a strongly bound form of benzene with a broad peak centered at 4.9 eV. Both species show a strong peak at 0.75 eV, which is an overtone of adsorbed benzene. However, the UV/HREELS spectra of the two species are quite different which is strong evidence that there are two forms of benzene on the surface.

We assign the weakly bound species to undistorted benzene. Figure 5 shows a UV spectrum of benzene. Our high-coverage spectra look very similar to the UV spectrum of benzene. Table 2 compares our peak positions to those of benzene. The peaks at 4.71, 6.20, and 6.84 eV in our spectra are also seen in the gas-phase UV spectrum of benzene [22–24]. We observe an extra peak at 3.82 eV. This peak is also seen in the electron loss spectrum of gas-phase benzene [25] and is associated with a UV forbidden transition. We observe the same peaks as in benzene. Therefore, we conclude that our weakly bound species is undistorted benzene.

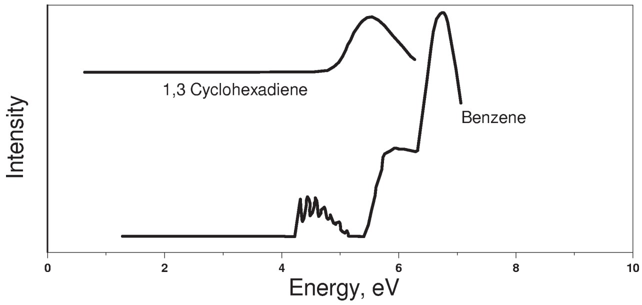

Figure 5. The UV spectrum of benzene [22] and 1,3-cyclohexadiene [23] replotted on a voltage scale.

In contrast, our data show that the strongly bound species is not benzene. Our low-coverage UV/HREELS spectra do not look anything like that expected for benzene. All of the aromatic molecules in the UV atlas [22] and the Sadtler tables of UV spectra [23] show a three-peak pattern with a major peak between 6 and 7 eV. There is no evidence for such a peak in figure 3. The UV/HREELS spectra provide clear evidence that the low-coverage species is not benzene. In fact, it is probably not aromatic.

The vibrational spectrum also suggests that the benzene is highly distorted. This is a little bit of an awkward issue, because our spectrum looks very similar to that previously assigned to chemisorbed undistorted benzene [7–9], and there is good agreement between the tables of vibrational frequencies in Ibach's book [26], and our data. However,

Table 1
A comparison of the vibrational spectra measured here to those of benzene and cyclohexadiene. Only IR or Raman active modes are included.[a]

	Benzene [12]	Benzene on Pt(111) [8]	0.4 L benzene on Pt(110) [this work]	1,4-cyclohexadiene [12]	1,3-cyclohexadiene [12]
M–C	992 (R)	360	335		
		570	425		
C–C deformations			560	615	698
		NR	1000	971	
C–C stretch	1483 (IR)	1310	1302	1300	1290
	1596 (IR)	1410	1383	1410	1410
			1457	1460	1460
C–H bend	673 (IR)	830	640	647	670
	849 (R) (w)	930	814	880	926
	1037 (IR)	1130	926	930	1165
	1178 (R)		1132	1160	
Combination bands	1815 (IR)		1634 (w)	1650	1704
	1960 (IR)				
OH stretch	3020 (IR)	3000	2955	2977	2884
	3047 (R, IR)		3021	3027	3050
	3062 (R)				
	3063 (IR)				

[a] (IR): IR active, (R): Raman active.

Table 2
A comparison of the UV/HREELS spectra of benzene to the UV spectrum of benzene and 1,4-cyclohexadiene [22–24].

0.4 L of benzene on Pt(110) [this work]	1,3-cyclohexadiene [22,23]	Benzene [22,24]	1 L of benzene on Pt(110) [this work]
4.9 eV	5.52 eV	6.88 eV	6.84 eV
		6.20 eV	6.20 eV
		4.70 eV	4.71 eV
		3.89 eV (EELS only)	3.82 eV

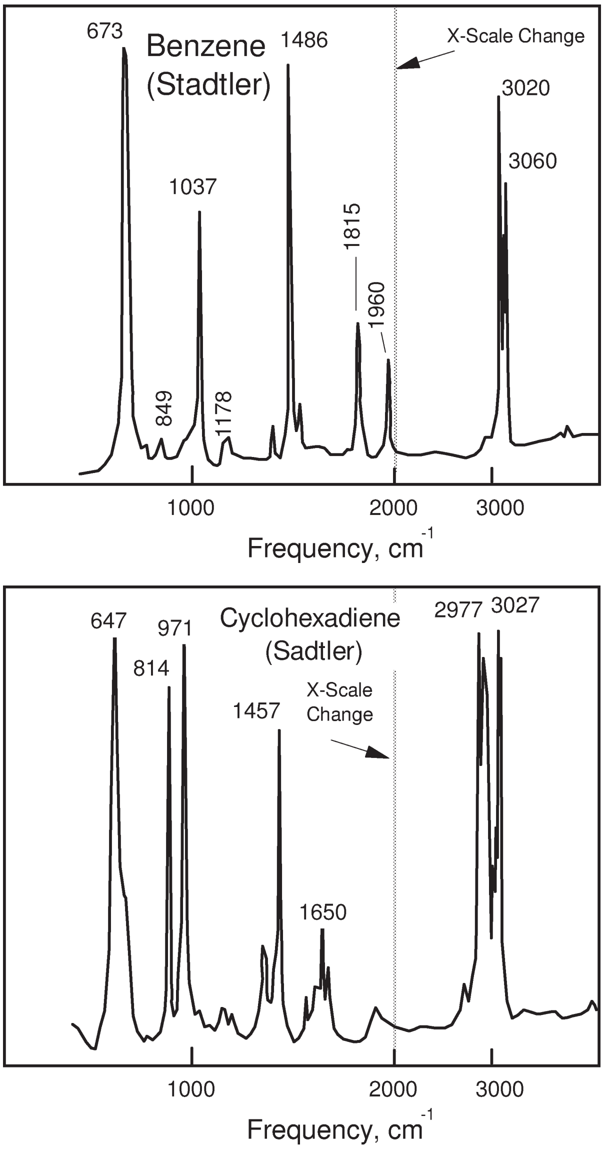

Figure 6. A replot of the IR spectrum of benzene and 1,4-hexadiene from the Sadtler tables [12].

Ibach's tables disagree with the Sadtler Handbook of IR spectra [12] and the Aldrich tables of IR frequencies [13]. Figure 6 shows a trace of the IR spectrum of benzene from the Sadtler tables. Notice that benzene shows strong modes at 1815 and 1960 cm^{-1}. Those modes are missing from our spectrum of 0.4 L of benzene on Pt(110). Benzene does not show any modes between 2800 and 3000 cm^{-1}. However, our spectrum of benzene on Pt(110) shows a clear peak in that region. Further, the pattern of peak intensities for our 0.4 L spectrum is different from the pattern for benzene.

Admittedly, the 1815 and 1960 cm^{-1} bands could be attenuated because of a selection rule. However, (2×1)Pt(110) is a highly corrugated surface. Zebisch et al. [15] found that benzene lies parallel to the (111) facets on (2×1)Pt(110). If Zebisch is right, the 1815 and 1960 modes in a benzene molecule should not be highly attenuated on Pt(110).

Our contention, therefore, is that the 1815 and 1960 cm^{-1} should be visible if the benzene molecule is still aromatic at low coverages on (2×1)Pt(110). The fact that the 1815 and 1950 cm^{-1}can no longer be seen is evidence that benzene undergoes some major changes when it adsorbs at low coverages on Pt(110).

We have searched the literature for other possibilities and, if we go back to Wander et al., we note that Wander proposed that the bonds in benzene distort to something which is close to the structure of 1,3-cyclohexadiene. Figure 5 shows a UV spectrum of 1,3-cyclohexadiene from the Sadtler tables [23] and that spectrum looks very similar to the spectrum in figure 3. Therefore, the UV/HREELS spectroscopy is consistent with Wander's suggestion that at low coverage the benzene undergoes major distortions. The UV/HREELS spectra are most consistent with formation of a diene.

The vibrational spectra are consistent as well. Figure 6 shows a replot of the IR spectrum of benzene and 1,3-hexadiene from the Sadtler tables [12]. We observe peaks in approximately the same peak positions as 1,3-cyclohexadiene and the pattern of peak intensities is also similar. A comparison of our spectrum in figure 4 to the spectra of benzene and of 1,3-cyclohexadiene in figure 6 shows that the cyclohexadiene IR spectrum fits the vibrational data for benzene on Pt(110) much better than the IR spectrum of benzene. Table 1 compares our vibrational spectra to those of 1,3- and 1,4-cyclohexadiene, and both show excellent agreement. Therefore, we conclude that Wander et al. were correct: at low coverages, benzene undergoes major distortions. We identify the distortions as a dienyl structure. Wander et al. did not call the structure a diene; however, their geometry is consistent with a diene.

Such a result does not imply that Horsley et al. are wrong, however. Note that Horsley et al. based their conclusions that the benzene was undistorted by examining the behavior of the 1s → $2p^*$ transition in NEXAFS. To put that in perspective, the 6.84 eV feature in figure 2 corresponds to a 2p → $2p^*$ transition. Notice that the 6.84 eV peak is not present below 0.4 L exposures. Horsley et al. would not have detected the low-coverage form of benzene since they were looking at a transition that does not occur at low coverages. Consequently, Horsley et al. would have detected only the high-coverage form of benzene in their experiments. The results here show that the high-coverage form of benzene is largely undistorted, in agreement with Horsley's measurements.

5. Conclusion

In summary then, in this paper we find that even though Wander et al. and Horsley et al. seem to reach contradictory conclusions, Wander et al. and Horsley et al. are both right. There are two forms of benzene on Pt(110): a low-coverage form which is highly distorted as suggested by Wander et al. and a high-coverage form which is essentially undistorted benzene as suggested by Horsley et al. We associate the low-coverage form of benzene with a dienyl structure, while the high-coverage form looks aromatic. These results show that apparently contradictory results can be rationalized when multiple species exist on a surface.

Acknowledgement

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