Surface Science Letters

Monolayer and multilayer films of nitrobenzene on Au(1 1 1) surfaces: bonding and geometry

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Abstract

We have investigated the interaction of nitrobenzene ($C_6H_5NO_2$) with a Au(1 1 1) surface. Nitrobenzene adsorbs molecularly and reversibly on Au(1 1 1) at 90 K. Three peaks occur in temperature programmed desorption at 290, 210 and 195 K due to desorption from the monolayer, bilayer and multilayer (as measured at low coverage for each phase). We report the infrared reflection–absorption spectra (IRAS) of nitrobenzene at submonolayer, monolayer and multilayer coverages. In the monolayer, nitrobenzene adsorbs with its molecular plane parallel to the surface and only two, out-of-plane molecular vibrations are observed in IRAS. In thicker films grown at 90 K, nitrobenzene molecules in the next several layers have an overall preferential orientation toward being parallel with the Au(1 1 1) surface plane. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Bonding of aromatic molecules with metal surfaces has been studied in surfaces science for the past 10–15 years [1–6]. Benzene (C_6H_6) adsorbs on most metal surfaces in a "flat-lying" geometry with the molecular plane parallel to the surface [1–3]. The nature of metal–benzene bonding can be described by donation of the π-electrons of the aromatic ring to unfilled orbitals of the metal, and back-donation of filled, metal orbitals into molecular π* states. In the case of monosubstituted

benzenes, as well as benzene heterocycles, surface bonding is a competition between the π-electron donation and electron donation by the substitutent atom or group. This can affect the orientation of the molecule, changing it from "flat lying" to tilted or perpendicular [2,7] to the surface plane. On Au(1 1 1) surfaces in particular, benzene [8], iodo-benzene (C_6H_5I) [9] and biphenyl (C_6H_5–C_6H_5) [9] adsorb with their molecular plane parallel to the surface. However, we showed recently that adsorbed phenyl groups on Au(1 1 1) adsorb with the molecular plane perpendicular to the Au(1 1 1) surface plane [8] because of the formation of a covalent σ-bond to the surface.

In contrast, molecules such as NO_2, N_2O_3, N_2O_4 [10,11] and CH_3NO_2 [12] adsorb on the Au(1 1 1) surface with the molecular planes perpendicular

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to the surface forming either one (for N_2O_3, CH_3NO_2, and N_2O_4) or two (for NO_2) O-surface bonds. These observations make nitrobenzene and interesting molecule to study because it combines the electron donating aromatic ring, which usually lies flat on the surface, and a strong electron donating (with respect to Au bonding) NO_2 group, which prefers to bind perpendicular to the surface. In addition to our fundamental interests, studies of the nitrobenzene–gold interaction are relevant to developments in supported-gold nanocluster catalysts [13–15] and formation of self-assembled monolayers (SAMs) on Au surfaces [16–19].

While there are reports concerning the interaction of organic molecules with gold surfaces [20–23], no studies have been reported previously for nitrobenzene ($C_6H_5NO_2$) adsorbed on Au single crystal surfaces. Nitrobenzene has been reported to decompose on Cu(1 1 0) and Cu(1 0 0) surfaces [24,25]. On the Cu(1 0 0) surface, decomposition forms nitrosobenzene and phenylnitrene [25], and is enhanced by Ni and hindered by Ag-overlayers. Nitrobenzene adsorbed on Ni(1 1 1) surfaces has also been studied by Raman spectroscopy [26–28].

In this letter, we report temperature programmed desorption (TPD) and Fourier-transform infrared reflection–absorption spectroscopy (IRAS) studies of nitrobenzene adsorbed on a Au(1 1 1) surface.

2. Experimental methods

Experiments were performed in a stainless steel UHV chamber equipped for AES, LEED, TPD and IRAS studies. The system had a base pressure of 2×10^{-10} Torr. The Au(1 1 1) crystal could be resistively heated to 1000 K and cooled to 87 K by direct contact of the copper block of the sample holder with liquid nitrogen. The Au(1 1 1) surface was cleaned by cycles of Ar^+ ion sputtering (0.5 keV, $P_{Ar} = 6 \times 10^{-5}$ Torr, $I_{sample} = 1.5$ µA) with the sample held at 450–500 K for 5 min and annealing in UHV at 1000 K for 10 min. This procedure resulted in a clean, well-ordered Au(1 1 1) surface which showed the ($\sqrt{3} \times 22$) reconstruction of the surface in LEED [29]. No surface carbon was detected by AES.

Nitrobenzene (Aldrich, 99+%) was degassed before dosing by several freeze–pump–thaw cycles that were carried out using the gas-handling line on the chamber. Nitrobenzene was introduced into the UHV chamber through a leak valve connected to a microcapillary-array doser. The gas exposures reported herein are uncorrected for ion gauge sensitivity or doser enhancement of the flux.

TPD measurements were made with the Au(1 1 1) crystal placed in line-of-sight of the mass spectrometer ionizer at a location that was 2 mm in front of the entrance aperture (10-mm diameter) of the shield covering the ionizer. A heating rate of 2.5 K/s was used.

IRAS was carried out at a grazing incidence angle of 86° from the surface normal. An Infinity® 60M FTIR spectrometer and a medium-band, liquid nitrogen cooled, mercury cadmium telluride (MCT) detector was used for collecting the IR spectra. Typically, spectra were taken at a spectrometer resolution of 4 cm^{-1} and by averaging 1000 scans taken over 5 min. All of the spectra reported were taken with a sample temperature of 87–90 K, and ratioed against the clean surface spectrum as a background.

The IR spectrum of liquid nitrobenzene (trapped between two KBr disks) was obtained with the same spectrometer described above, but using a wide-band, liquid-nitrogen cooled, MCT detector. The spectra were taken in the transmission mode at a spectrometer resolution of 1 cm^{-1} by averaging 10 scans over 12 s.

3. Results and discussion

3.1. Temperature programmed desorption

Nitrobenzene was the only desorption product detected in TPD after nitrobenzene adsorption on the Au(1 1 1) surface at 90 K. In particular we looked for nitrogen oxide (NO) (30 amu), nitrogen dioxide (NO_2) (46 amu), biphenyl ($C_6H_5–C_6H_5$) (154 amu), and C_6H_6 (78 amu). No signals were detected other than those expected from cracking of nitrobenzene molecules in the QMS. As shown in Fig. 1, nitrobenzene TPD spectra exhibited three desorption peaks. First, at low coverage,
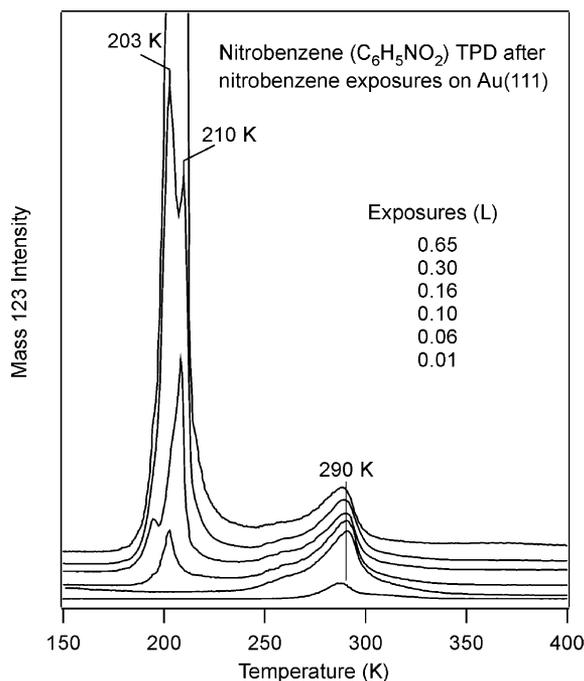
Fig. 1. $C_6H_5NO_2$ TPD spectra after $C_6H_5NO_2$ exposures on Au(1 1 1) at 90 K.

there is a peak at 290 K. The second peak grows in at higher coverage at 210 K, followed by a third peak at 203 K. We observed a similar TPD pattern for benzene (C_6H_6) [8] and iodobenzene (C_6H_5I) [9] desorption from the Au(1 1 1) surface. There, we assigned the origin of these three desorption peaks to desorption from the monolayer, second layer, and multilayer. Desorption of physisorbed molecules from the second layer in a peak that is distinct from subsequent physisorbed layers is a common feature for the desorption of aromatic molecules from Au(1 1 1) and Cu(1 1 1) surfaces [8,9,30,31].

In this paper, $C_6H_5NO_2$ coverage Θ is defined as $\Theta = 1$ ML by the saturation value for the area under the $C_6H_5NO_2$ TPD peak at 290 K. We estimate that this corresponds to a molecular density of about 1.9×10^{14} cm^{-2} based on hexagonal close-packed molecules with van der Waals contact distances.

Using Redhead analysis, and assuming first-order desorption kinetics with a preexponential factor of 10^{13} s^{-1}, the $C_6H_5NO_2$ desorption acti-

vation energy (E_d) can be estimated to be 18 and 13 kcal/mol for the first and second adsorbed layers, respectively. Because there is typically no appreciable barrier to molecular adsorption, these values for E_d are good estimates of the respective adsorption energies of $C_6H_5NO_2$ on Au(1 1 1).

3.2. Infrared reflection–absorption spectroscopy

Only two absorption bands at 710 and 793 cm^{-1} appear in the IR spectra of nitrobenzene at sub-monolayer and monolayer coverages on Au(1 1 1), as shown in Fig. 2. More bands appear in the spectra with increasing $C_6H_5NO_2$ coverage, and 10 vibrational bands are detected for a 10 ML film. To confirm the vibrational assignments, as well as to measure the relative intensities of some vibrational bands, the spectrum of a thick condensed
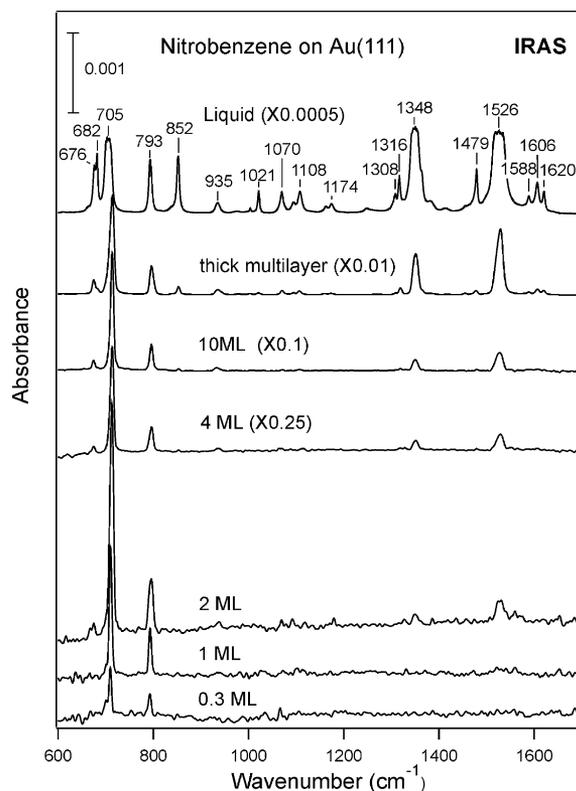

Fig. 2. IRAS spectra of $C_6H_5NO_2$ adlayers on Au(1 1 1) at 90 K. The IR spectra of liquid-phase $C_6H_5NO_2$ is also provided for comparison.

film of nitrobenzene (∼100 ML thick) was also taken. Assignment of the vibrational modes for adsorbed nitrobenzene was made by comparisons to the vibrational assignments for liquid nitrobenzene [34]. The IR spectrum for liquid nitrobenzene is shown in Fig. 2 and the mode assignments are given in Table 1. Nitrobenzene has a planar molecular structure with C_{2v} symmetry [32]. The molecule has 36 normal modes, which are classified by the following symmetry types: $\Gamma_v = 13A_1 + 4A_2 + 7B_1 + 12B_2$. Symmetry types A_1 and B_2 correspond to in-plane vibrations, and symmetry types A_2 and B_1 correspond to out-of-plane vibrations. In the nitrobenzene spectra at submonolayer coverage, the band at 710 cm^{-1} corresponds to mode 21, an NO$_2$ out-of-plane bending mode with B_1 symmetry, and the band at 793 cm^{-1} corresponds to mode 20, a C–H out-of-

Table 1
Vibrational frequencies (cm^{-1}) and mode assignments for IR spectra of nitrobenzene ($C_6H_5NO_2$)

Symmetry representation in C_{2v}	Mode no.	Type of mode	Liquid [34]	Adsorbed on Au(111)				
				∼100 ML	10 ML	4 ML	2 ML	1 ML
A_1	1	vCH	3111	3110				
	2	vCH	3082	3077				
	3	vCH	3049	3029				
	4	vCC	1586	1588				
	5	vCC	1480	1478	1478			
	6	v_sNO$_2$	1346	1350	1350	1350	1350	
	7	βCH	1173	1173				
	8	vC–NO$_2$	1107	1106	1106			
	9	βCH	1021	1021				
	10	Ring	1003	1003				
	11	δNO$_2$	852	853		853	853	
	12	αC–C–C	680	682				
	13	αC–C–C	394					
A_2	14	γCH	975	978				
	15	γCH	840					
	16	ϕCC	394					
	17	Torsion	–					
B_1	18	γCH	990					
	19	γCH	935	935	933	935		
	20	γCH	794	796	796	796	793	793
	21	γNO$_2$	704	714	714	714	713	710
	22	ϕCC	675	675	674	674	675	
	23	ϕCC	420					
	24	γC–NO$_2$	176					
B_2	25	vCH	3093					
	26	vCH	3031					
	27	vCC	1590	1588				
	28	v_{as}NO$_2$	1524	1529	1528	1528	1528	
	29	vCC	1458	1454				
	30	vCC	1317	1318	1319			
	31	βCH	1308	1308				
	32	βCH	1161	1159				
	33	βCH	1070	1071	1071			
	34	αCCC	611					
	35	rNO$_2$	530					
	36	βC–NO$_2$	254					

v – stretching; v_s – symmetric stretching; v_{as} – asymmetric stretching; β – in-plane band; γ – out-of-plane band; α – in-plane ring deformation; ϕ – out-of-plane ring deformation; r – rocking; δ – symmetric deformation.

plane bending mode with B_1 symmetry. In thicker films, the bands at 1528 and 1350 cm^{-1} are assigned to NO$_2$-asymmetric stretching (v_{as}NO$_2$, B$_2$) and NO$_2$-symmetric stretching (v_sNO$_2$, A$_1$) modes, respectively. Absorption bands at 935, 853 and 674 cm^{-1} correspond to C–H out-of-plane bending (γCH, B$_1$), NO$_2$-symmetric deformation (δNO$_2$, A$_1$) and out-of-plane ring deformation (ϕCC, B$_1$) modes, respectively. These assignments are given in Table 1.

A distinct feature of the IR spectra of nitrobenzene at submonolayer and monolayer coverages is that the only two bands that are observed, at 710 cm^{-1} (γNO$_2$, B$_1$) and 793 cm^{-1} (γCH, B$_1$), are both out-of-plane modes. The three most intense absorption bands in the IR spectra of liquid nitrobenzene (as shown in Fig. 2) are due to γNO$_2$ (B$_1$), v_sNO$_2$, (A$_1$), and v_{as}NO$_2$, (B$_2$) modes. The intensities of these modes are very similar. Thus, the absence of v_sNO$_2$ and v_{as}NO$_2$ bands in the IR spectra of C$_6$H$_5$NO$_2$ at monolayer coverage must be because of a specific molecular orientation at the surface, rather than a lack of sensitivity for

detecting these modes. The surface selection rule [33] states that dynamic dipoles parallel to the surface are very strongly screened such that those corresponding modes are not observed. For adsorption in a "flat-lying" orientation with the molecular plane parallel to the surface plane (Fig. 3a), only vibrational modes with A$_2$ and B$_1$ symmetry will be observed in the IRAS spectra. On this basis, we conclude that nitrobenzene adsorbs on Au(1 1 1) with the molecular plane parallel to the surface at monolayer and submonolayer coverages. The other modes with A$_2$ or B$_1$ symmetry were too low in intensity at these coverages to be detected in these spectra.

The appearance of bands due to modes with A$_1$ and B$_2$ symmetry in the nitrobenzene spectra at coverages exceeding 1 ML is due to a change in molecular orientation. Neither in-plane nor out-of-plane modes are screened completely. Thus, completely oriented films with only either parallel (Fig. 3a) and perpendicular (Fig. 3b) orientations of molecules in these thicker films must be excluded. Assuming adsorption in a "tilted"
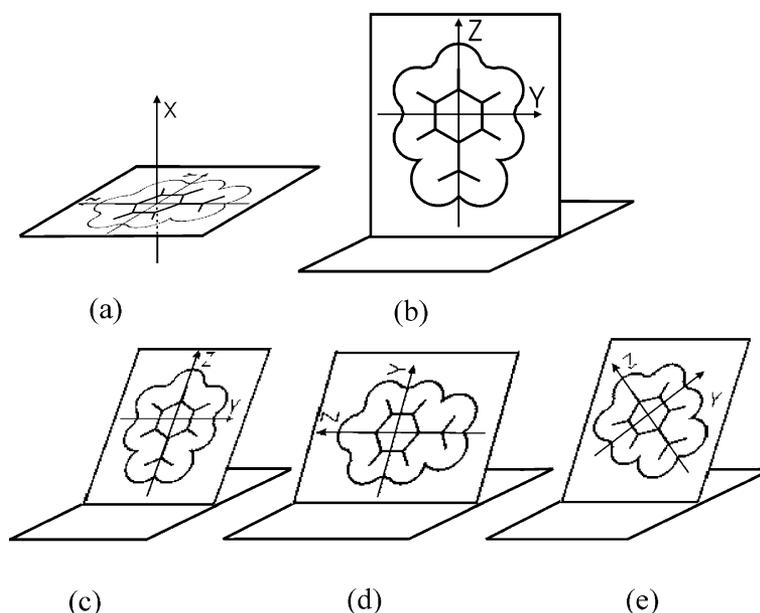

Fig. 3. Orientations of nitrobenzene adsorbed on Au(1 1 1) surfaces: (a) "parallel", with the molecular plane parallel to the surface plane, (b) "perpendicular", with the molecular plane perpendicular to the surface plane, (c) "tilted", with the Y axis parallel to the surface and the molecular plane tilted, (d) "tilted", with the Z axis parallel to the surface and the molecular plane tilted, and (e) "tilted", with molecular Z and Y axes both tilted with respect to the surface plane.

orientation, with the molecular plane tilted with respect to the surface plane, Fig. 3 depicts three possibilities for "tilted" orientations: molecular Y-axis parallel to the surface plane (Fig. 3c), molecular Z-axis parallel to the surface plane (Fig. 3d), and molecular Y and Z axes tilted with respect to the surface plane (Fig. 3e). We can distinguish between these three possibilities by looking for the bands due to $v_s NO_2$, (A_1) and $v_{as} NO_2$, (B_2) modes in the spectra. The dynamic dipoles of $v_s NO_2$ and $v_{as} NO_2$ modes change along with the molecular Z-axis and Y-axis, respectively. Because of the surface selection rule, the appearance of both of these modes in the spectra excludes orientations with the molecular Z-axis or Y-axis parallel to the surface (Fig. 3c and d). The only possible "tilted" orientation is one where both of the molecular Z and Y axes are tilted with respect to the surface plane (Fig. 3e).

The relative intensities of the $v_s NO_2$ (A_1) and $v_{as} NO_2$ (B_2) bands compared to that of the γNO_2 (B_1) band in nitrobenzene spectra at multilayer coverages are not constant and gradually increase with the coverage. This change is shown in Fig. 4.
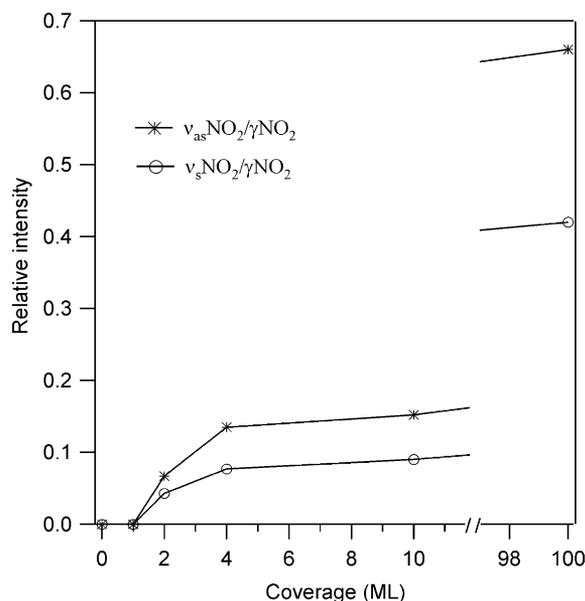

Fig. 4. Relative absorption intensities of the NO_2 symmetric $(v_s NO_2)$ and asymmetric $(v_{as} NO_2)$ stretching bands compared to the NO_2 out-of-plane bending (γNO_2) band in IR spectra for increasing nitrobenzene coverages on Au(1 1 1) at 90 K.

This indicates that the angle between the nitrobenzene molecular plane and the surface plane also increases gradually with the coverage. We conclude that a change from a "flat lying" to "tilted" orientation occurs only gradually as thicker films are grown on Au(1 1 1) at 90 K. Nitrobenzene molecules at coverages between 1 and 2 ML retain an adsorption geometry such that the ring plane is close to parallel with the surface plane.

4. Conclusion

Nitrobenzene reversibly adsorbs on the Au(1 1 1) surface under UHV conditions. Three molecular desorption peaks occur at 290, 210 and 203 K, corresponding to desorption from the chemisorbed monolayer and physisorbed second-layer and multilayer, respectively. The desorption activation energy was estimated to be 18 and 13 kcal/mol for the monolayer and second layer, respectively. This strongly bound, chemisorbed state is characterized by an adsorption geometry with the molecular plane parallel to the surface, in a "flat-lying" orientation. For higher coverages, i.e., thicker films, the average molecular orientation changes gradually from one with the molecular plane nearly parallel to the surface to orientations with an increasing degree of tilt of the molecular Z and Y axes tilted with respect to the Au(1 1 1) surface.

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