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Adsorption of iodobenzene (C_6H_5I) on Au(1 1 1) surfaces and production of biphenyl ($C_6H_5-C_6H_5$)

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Abstract

Thermal decomposition of alkyl halides has been widely used for generating adlayers of hydrocarbon species or fragments on metal surfaces. We investigated the possibility of using the thermal dissociation of iodobenzene (C_6H_5I) as a method for generating chemisorbed phenyl groups bound to Au(1 1 1) surfaces. Iodobenzene desorbs molecularly in three peaks at 290–308, 212 and 188 K in temperature programmed desorption (TPD) and partially decomposes at 200–250 K to form coadsorbed biphenyl and iodine on the surface. Biphenyl species produced from C_6H_5I decomposition, or from gas-phase biphenyl dosing, are chemisorbed reversibly and molecularly, with the molecular plane parallel to the surface. These strongly chemisorbed species do not desorb until 400 K. Iodine desorption at 720 K leaves a clean Au(1 1 1) surface following TPD of C_6H_5I adlayers. Carbon–iodine (C–I) bond dissociation to produce phenyl groups (C_6H_5) occurs at a higher temperature than that required for phenyl–phenyl coupling reactions. Thus, we do not detect the formation of adsorbed, isolated phenyl groups from iodobenzene thermal dissociation on the Au(1 1 1) surface. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Aromatics; Gold; Thermal desorption; Infrared absorption spectroscopy; Vibrations of adsorbed molecules

1. Introduction

Preparation and characterization of well-defined hydrocarbon species on metal surfaces is an important aspect of elucidating the surface science of catalysis. Thermal decomposition of alkyl halides is a common method for generating alkyl species on metal surfaces [1]. The thermal chemistry of iodobenzene (C_6H_5I) has been investigated previously on Ag(1 1 1) [2,3], Cu(1 1 1) [4,5], Pt(1 1 1) [6] and Pd(1 1 1) [7] surfaces. Submonolayer cov-

erages of C_6H_5I have been reported to dissociate to form coadsorbed iodine atoms and phenyl (C_6H_5) groups on the surface, with chemisorbed phenyl stable on Ag(1 1 1) and Cu(1 1 1) surfaces up to at least 300 K [3–5]. C_6H_5I thermal chemistry on Pt(1 1 1) leads to different products than described above. Phenyl groups formed after carbon–iodine (C–I) bond cleavage at 175 K undergo further disproportionation reactions to form *ortho*- C_6H_4 (benzyne) groups and hydrogen adatoms on the surface. Upon further heating, adsorbed benzyne groups undergo both rehydrogenation to form benzene and decomposition to form surface carbon and desorb molecular hydrogen. On Pd(1 1 1), iodobenzene decomposes to form benzene, iodine, carbon, and hydrogen.

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Electron-induced dissociation (EID) of symmetrical hydrocarbons is another technique that has been used for such purposes [8–11]. In particular, we demonstrated that EID of benzene adlayers on Au(111) at 90 K can cleanly generate chemisorbed phenyl groups bonded to the surface [12]. Phenyl groups formed in this way stay bound to the surface and undergo no thermal reaction until 165 K. At higher temperatures, phenyl group coupling forms adsorbed biphenyl ($C_6H_5-C_6H_5$) which desorbs from the surface near 400 K.

In this paper we report on the thermal chemistry of iodobenzene on the Au(111) surface. Our purpose was to investigate the possibility of using thermal dissociation of C–I bonds in iodobenzene to cleanly form chemisorbed phenyl groups. Our approach was to compare the temperature programmed desorption (TPD) and infrared reflection absorption spectroscopy (IRAS) data for surface species, i.e., adsorbed phenyl groups and biphenyl molecules generated both by EID of benzene and iodobenzene thermal decomposition. We find that iodobenzene is largely reversibly adsorbed on the Au(111) surface, with three molecular desorption peaks at 290–308, 211 and 185 K corresponding to desorption of the iodobenzene monolayer, second layer and multilayer, respectively. Iodobenzene partially decomposes between 200 and 250 K to form iodine and adsorbed biphenyl on the surface, with no appreciable concentration of adsorbed phenyl groups due to rapid C–C coupling reactions.

2. Experimental methods

Experiments were performed in a stainless steel UHV chamber equipped for Auger electron spectroscopy (AES), low energy electron diffraction (LEED), TPD and Fourier-transform infrared (FTIR) spectroscopy studies, as described previously [13]. The system had a base pressure of 6×10^{-10} Torr. The Au(111) 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(111) surface was cleaned by cycles of Ar^+ ion sputtering (0.5 keV, $P_{Ar} = 6 \times 10^{-5}$ Torr, $I_{sample} = 1.5 \mu A$) with

the sample held at 450–500 K for 8 min and annealing in UHV at 1000 K for 20 min. This procedure resulted in a clean, well-ordered Au(111) surface which showed the $(\sqrt{3} \times 22)$ reconstruction of the surface [14] in LEED. No surface carbon was detected by AES.

Iodobenzene (C_6H_5I) (Aldrich, 99+%) was degassed before dosing by several freeze–pump–thaw cycles that were carried out using the gas-handling line on the chamber. Iodobenzene and biphenyl ($C_{12}H_{10}$) (J.T. Baker, practical purity) were 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(111) crystal placed in line-of-sight of the mass spectrometer ionizer at a location of 2 mm in front of the entrance aperture (10 mm diameter) of the shield covering the ionizer. A heating rate of 3.3 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 detector was used for collecting the IR spectra. Spectra were taken typically at a spectrometer resolution of 4 cm^{-1} and by averaging 1000 scans taken over 5 min. All of the spectra reported, even those that were obtained during “warm-up” studies, were taken with a sample temperature of 87–90 K and ratioed against the clean surface spectrum as a background.

3. Results and discussion

3.1. Temperature programmed desorption

Iodobenzene, biphenyl and iodine were the only desorbed products detected in TPD after iodobenzene adsorption on the Au(111) surface. Figs. 1 and 2 present the TPD spectra of iodobenzene (at 204 amu) and biphenyl (at 154 amu) evolving from the Au(111) surface as a function of iodobenzene exposure. Iodine desorbs from the surface at 720 K as shown in Fig. 3. C_6H_5I TPD spectra from the Au(111) surface exhibit three desorption

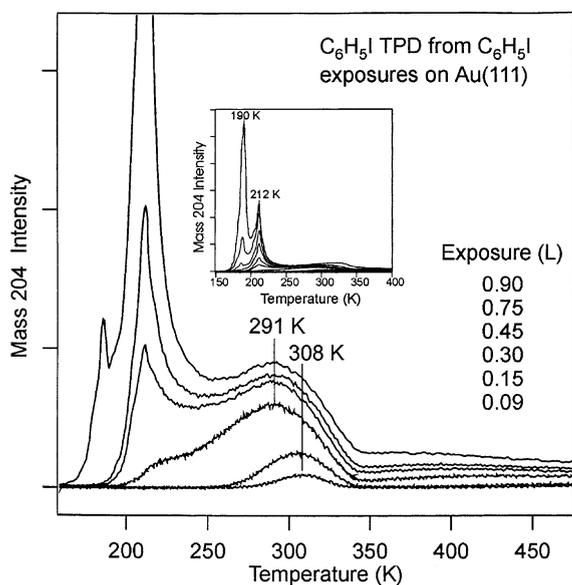


Fig. 1. Iodobenzene (C_6H_5I) TPD spectra after C_6H_5I exposures on Au(1 1 1) at 90 K.

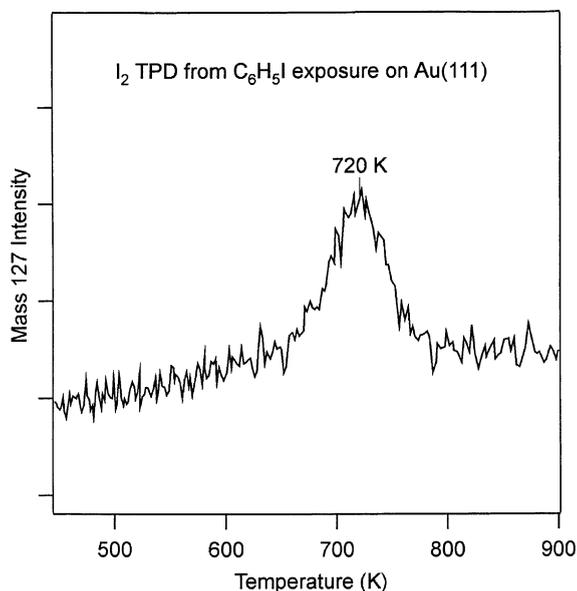


Fig. 3. I_2 TPD spectra after C_6H_5I exposures on Au(1 1 1) at 90 K.

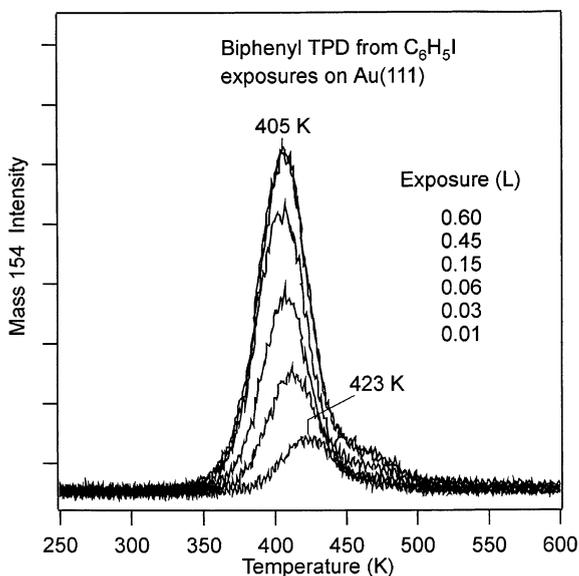


Fig. 2. Biphenyl ($C_6H_5-C_6H_5$) TPD spectra after C_6H_5I exposures on Au(1 1 1) at 90 K.

peaks. First, at low coverages, a broad desorption peak occurred at 290–308 K. A second peak was then formed at 212 K, followed by a third peak at 188 K.

In related studies, TPD traces after C_6H_5I adsorption on Cu(1 1 1) at the highest coverages also showed two molecular desorption peaks at 200 and 185 K, which were assigned as second-layer and multilayer desorption, respectively [5]. These states of C_6H_5I can be compared to the desorption of benzene (C_6H_6) from the second layer (at 155 K) and multilayer (at 152 K) from Cu(1 1 1) [15]. No desorption of C_6H_5I from the monolayer on Cu(1 1 1) occurred because the chemisorbed layer irreversibly dissociated at 175 K to form iodine adatoms and phenyl species bound to the surface. Biphenyl desorption is a reaction-rate limited process on Cu(1 1 1) because desorption occurs at temperatures that are 30–50 K higher than desorption of molecularly adsorbed biphenyl which has been dosed directly.

On the Au(1 1 1) surface, only part of the iodobenzene monolayer dissociates. We assign the C_6H_5I TPD peak at 308 K to desorption of reversibly adsorbed C_6H_5I from the monolayer. C_6H_5I TPD peaks at 212 and 188 K are assigned to second-layer and multilayer desorption, respectively, analogous to that on Cu(1 1 1). Using Redhead analysis and assuming first-order desorption kinetics with a preexponential factor of

10^{13} s^{-1} , the $\text{C}_6\text{H}_5\text{I}$ desorption activation energy, E_d , can be estimated to be 19 and 12.9 kcal/mol for the first and second adsorbed layers, respectively. For sublimation from the multilayer, an Arrhenius plot of the desorption trace (making no assumption about the kinetic order) gives $E_d = 12.5$ kcal/mol. Because we expect no appreciable barrier to $\text{C}_6\text{H}_5\text{I}$ adsorption, values for E_d are good estimates of the respective adsorption energies for $\text{C}_6\text{H}_5\text{I}$ on Au(111) surfaces.

The saturation monolayer coverage, θ^{sat} , of iodobenzene and biphenyl ($\text{C}_6\text{H}_5\text{-C}_6\text{H}_5$) on Au(111) at 90 K can be estimated as 0.16 and 0.084 ML, respectively, by assuming a hexagonal close-packed, “flat-lying” adsorption geometry with van der Waals contacts (this orientation will be established below). We define the coverages reported herein relative to $\theta = 1$ ML for the surface Au atom density of 1.39×10^{15} atoms/cm² on Au(111).

To probe the influence of surface defects on the $\text{C}_6\text{H}_5\text{I}$ desorption peak at 305 K, we compared TPD spectra after $\text{C}_6\text{H}_5\text{I}$ adsorption on well-ordered and roughened surfaces, as shown in Fig. 4. Here, the surface was roughened by Ar^+ ion sputtering at 1 keV with the crystal at 300 K, with no subsequent annealing. The large increase in the number of surface defects produced by ion sputtering did not increase the size of the $\text{C}_6\text{H}_5\text{I}$ desorption peak at 291 K. Instead, this TPD peak almost disappeared and more iodobenzene desorbed near 400 K on the roughened surface. Using Redhead analysis and assuming first-order desorption kinetics with a preexponential factor of 10^{13} s^{-1} , E_d for $\text{C}_{12}\text{H}_{10}$ can be estimated to be 25 kcal/mol.

As shown in Fig. 2, the biphenyl yield in TPD increased proportionally to the $\text{C}_6\text{H}_5\text{I}$ exposure and saturated after a 0.6 L dose. Biphenyl is formed on the surface by C–C coupling of two phenyl groups formed after C–I bond dissociation in adsorbed iodobenzene. The C–I dissociation temperature for $\text{C}_6\text{H}_5\text{I}$ on Au(111) is expected to be between 200–300 K given that $\text{C}_6\text{H}_5\text{I}$ dissociates on Cu(111) at 175 K, because C–I bond dissociation for linear $\text{C}_2\text{-C}_4$ alkyl iodides occurs on Cu(111) below 120 K and on Au(111) above 200 K [16].

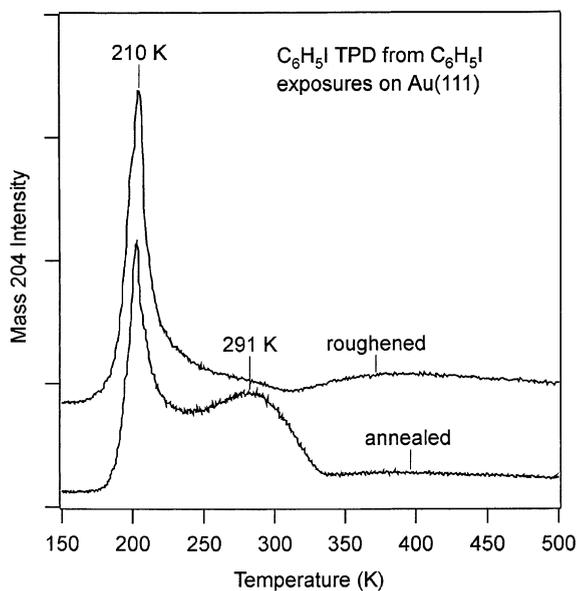


Fig. 4. $\text{C}_6\text{H}_5\text{I}$ TPD spectra after $\text{C}_6\text{H}_5\text{I}$ exposures on roughened (top curve) and annealed, highly ordered (bottom curve) Au(111) surfaces at 90 K.

Biphenyl evolution from the surface in TPD following $\text{C}_6\text{H}_5\text{I}$ exposures is a desorption-rate limited process. As shown in Fig. 5, biphenyl desorption after biphenyl molecules were dosed on Au(111) occurs at temperatures above 400 K at small coverages, and this is identical to the biphenyl desorption observed after iodobenzene reaction on the surface.

Fig. 6 displays the $\text{C}_6\text{H}_5\text{I}$ adsorption kinetics as an uptake curve that can be constructed from TPD curves after $\text{C}_6\text{H}_5\text{I}$ adsorption on Au(111) at 90 K. These uptake curves allow us to estimate the fraction of the $\text{C}_6\text{H}_5\text{I}$ monolayer that dissociates on the surface. The biphenyl curve in Fig. 6 was adjusted and converted to a $\text{C}_6\text{H}_5\text{I}$ – equivalent scale by forcing the biphenyl curve at low coverages (where biphenyl is the only product) to have the same slope as the $\text{C}_6\text{H}_5\text{I}$ curve corresponding to multilayer $\text{C}_6\text{H}_5\text{I}$ desorption. This procedure assumes (as is usually the case for such molecules [17]) that the sticking coefficient S has the same value for adsorption into both the monolayer and multilayer at 90 K. We estimate that $\sim 17\%$ of the chemisorbed $\text{C}_6\text{H}_5\text{I}$ monolayer ($\theta^{\text{sat}}(\text{C}_6\text{H}_5\text{I}) = 0.16$ ML) dissociates on Au(111) during TPD. This

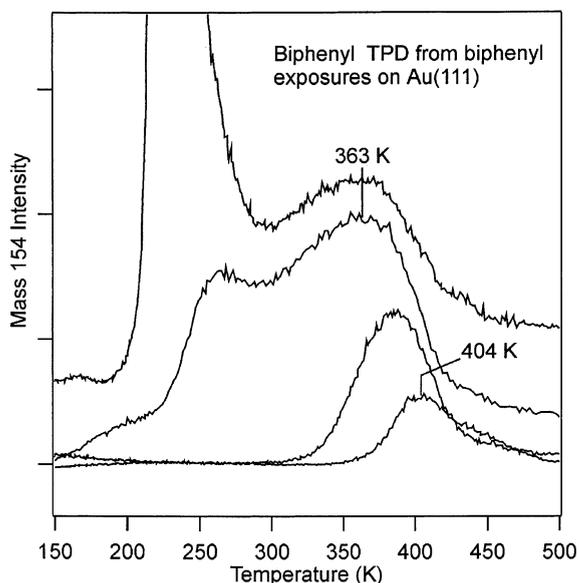


Fig. 5. Biphenyl ($C_6H_5-C_6H_5$) TPD spectra after biphenyl exposures on Au(111) at 90 K.

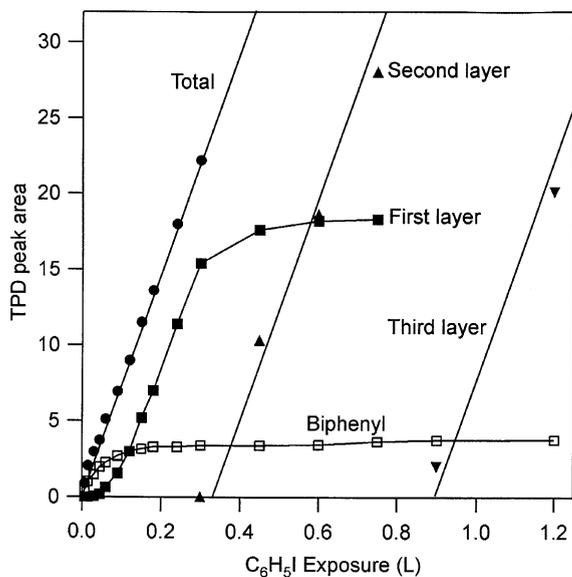


Fig. 6. Uptake curves of the adsorption kinetics and desorption products following iodobenzene exposures on Au(111) at 90 K. The plot was constructed using C_6H_5I and $C_6H_5-C_6H_5$ TPD peak areas. The curve corresponding to total uptake was constructed from the sum of iodobenzene TPD peak areas and twice the biphenyl TPD peak area for each exposure.

corresponds to the formation and desorption of 0.014 ML of $C_6H_5-C_6H_5$. An independent estimate of this amount can be made by comparing the biphenyl TPD peak area corresponding to monolayer coverage obtained after biphenyl dosing with the TPD peak area of biphenyl evolved following iodobenzene reaction. We found that this amounted to 24% of θ^{sat} ($C_6H_5-C_6H_5$) = 0.084 ML), i.e., 0.020 ML, consistent with the value of 0.014 ML found by using the other method.

3.2. Infrared reflection adsorption spectroscopy

Fig. 7 illustrates the IRAS spectra of C_6H_5I adsorbed on Au(111) at 90 K. Only two vibrational bands at 676 and 728 cm^{-1} were observed in the spectra taken at low coverages. Several new

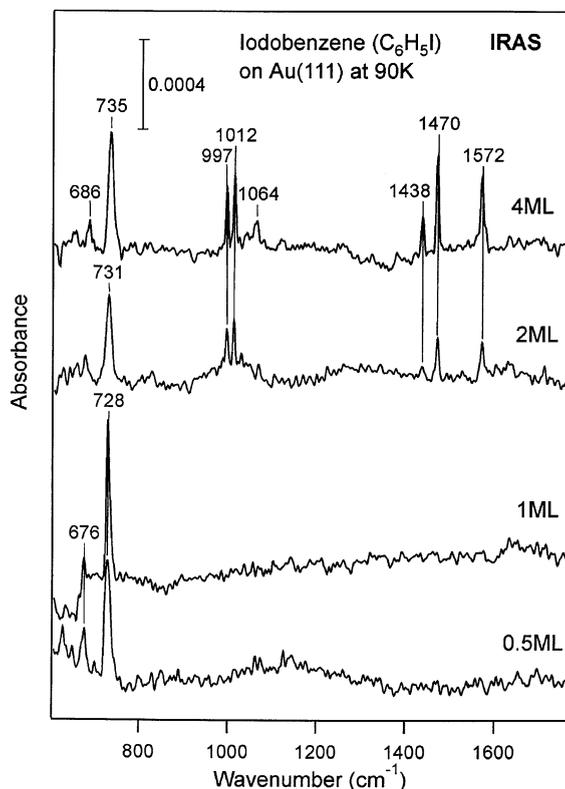


Fig. 7. IRAS spectra following iodobenzene (C_6H_5I) exposures on Au(111) at 90 K.

Table 1
Assignments of the vibrational spectra of iodobenzene (C_6H_5I)

Symmetric representation in C_{2v}	Type of mode	Liquid [23]	Multilayer		Monolayer	
			Au(111) (this work)	Cu(111) ^a [4]	Au(111) (this work)	Cu(111) ^a [4]
a_1	ν CH	3031	3052	3050		3030
	ν CC	1577	1572	1575		
	ν CC	1468	1470	1475		
	β CCCH	1175		1175		
	ν C–I	1060	1064			
	β CCCH	1015	1012			
	Ring breathing	997	997	1005		
a_2	γ CH	835				
b_1	γ CH	904		905		
	γ CH	729	735	720	728	710
b_2	χ CCC	681	686		676	
	ν CC	1435	1438			
	ν CC	1321		1315		
	β CCCH	1259				

ν : stretching; β : in-plane-bend; γ : out-of-plane band; χ : nonplanar twist.

^a HREELS data.

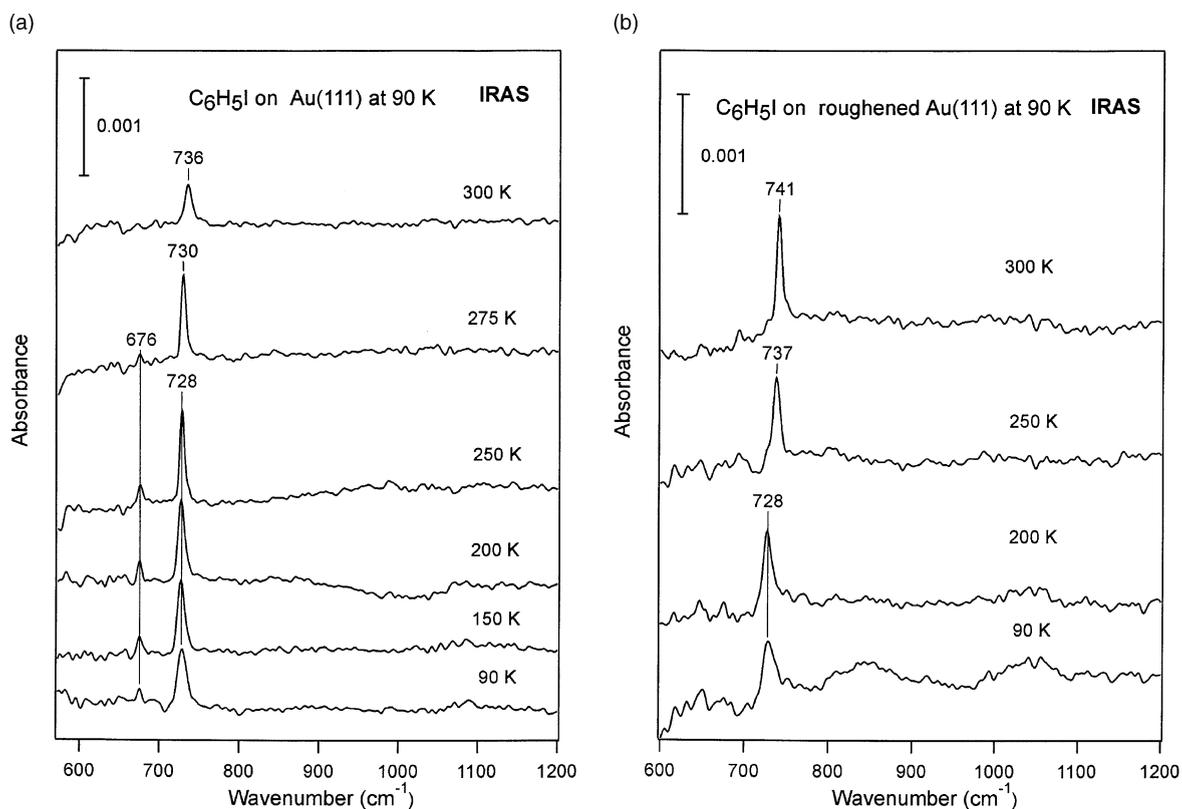


Fig. 8. IRAS “warm-up” spectra for a submonolayer coverage of C_6H_5I adsorbed on (a) annealed, well-ordered and (b) roughened Au(111) surfaces at 90 K.

bands in the 1000–1600 cm^{-1} region appeared in the spectra taken at higher coverages. The assignment of the spectra of adsorbed $\text{C}_6\text{H}_5\text{I}$ was made primarily by utilizing the vibrational assignments of iodobenzene in the liquid phase [23], as shown in Table 1. The vibrations observed at 676 and 728 cm^{-1} at submonolayer coverage and at 686 and 734 cm^{-1} at higher (multilayer) coverages correspond to non-planar twisting and C–H out-of-plane bending modes. Bands at 997, 1012, 1438, 1470 and 1572 cm^{-1} correspond to C–C–H in-plane bending and stretching modes.

The absence of peaks from in-plane vibrational modes in the IR spectra at submonolayer coverages and high relative intensities of these peaks at multilayer coverages can be explained by different orientations of iodobenzene molecules at different coverages. According to the surface-dipole selection rule [18], molecular vibrations with in-plane dynamic dipoles are screened by the surface for “flat-lying” molecular orientations that have the π -ring parallel to the surface. Such an orientation is common for benzene adsorbed at submonolayer coverages on metal surfaces [15,19–21]. Based on Fig. 7, $\text{C}_6\text{H}_5\text{I}$ molecules also adsorb on Au(111) in an orientation with their π -rings parallel to the surface plane at submonolayer and monolayer coverages. This is in contrast to behavior on the Cu(111) surface where it was concluded that $\text{C}_6\text{H}_5\text{I}$ and $\text{C}_6\text{H}_5\text{Cl}$ adsorb with the ring-plane tilted away from the surface plane by $45 \pm 5^\circ$ at submonolayer coverages [22]. Only at coverages exceeding one monolayer i.e., in multilayer films, are some $\text{C}_6\text{H}_5\text{I}$ molecules oriented on Au(111) with the molecular plane tilted with respect to the surface plane.

“Warm-up” studies using IRAS were conducted at submonolayer coverages in order to determine the temperature at which C–I bond scission occurs in the iodobenzene adlayer on Au(111). Defects on the Au(111) surface significantly enhanced C–I bond dissociation, and so we conducted one set of these warm-up experiments using well-annealed Au(111) surfaces and another set using highly defective Au(111) surfaces which were not annealed after Ar^+ ion sputtering. In these experiments, as shown in Fig. 8(a) and (b), the sample temperature was raised sequentially from 90 to 300

K, and then the sample was recooled to 90 K to collect the IR spectra. In both figures, for spectra at 90 K, there is a peak at 728 cm^{-1} corresponding to the C–H out-of-plane bending mode in adsorbed $\text{C}_6\text{H}_5\text{I}$ molecules. On the other hand, for spectra at 300 K, there is a peak at 736 and 741 cm^{-1} for annealed and roughened surfaces, respectively. This shift is an indicator of the formation of biphenyl ($\text{C}_6\text{H}_5\text{--C}_6\text{H}_5$). This identification of adsorbed biphenyl molecules comes from IRAS spectra, shown in Fig. 9, of molecularly adsorbed biphenyl on Au(111) at 90 K after dosing biphenyl molecules from the gas phase. The IRAS spectra for submonolayer coverages are almost

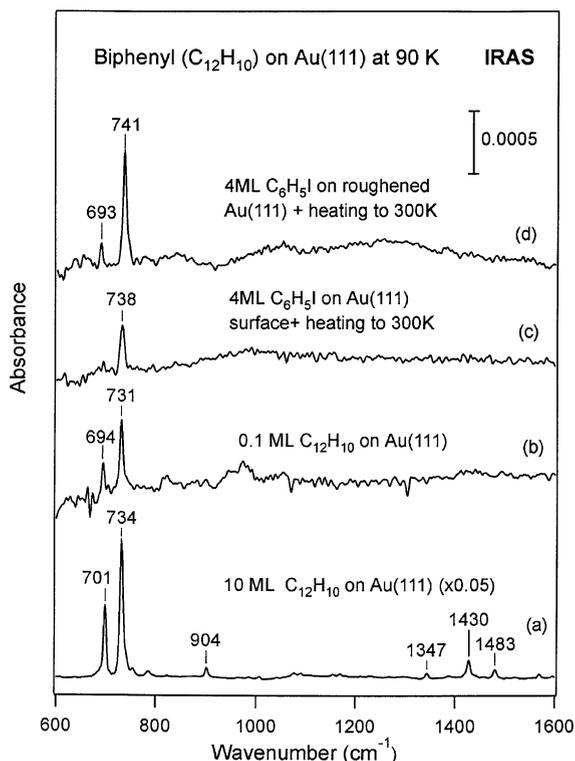


Fig. 9. Comparison of the IRAS spectra of adsorbed biphenyl ($\text{C}_6\text{H}_5\text{--C}_6\text{H}_5$) on Au(111) at 90 K produced in several ways: (a) dosing biphenyl to form a multilayer, (b) dosing biphenyl to submonolayer coverage, (c) adsorption and dissociation of a submonolayer coverage of $\text{C}_6\text{H}_5\text{I}$ on an annealed, well-ordered surface heated to 300 K, and (d) adsorption and dissociation of a submonolayer coverage of $\text{C}_6\text{H}_5\text{I}$ on a roughened surface heated to 300 K.

Table 2
Vibrational assignments for biphenyl (C₆H₅–C₆H₅)

Symmetric representation in D _{2h}	Type of mode	C ₁₂ H ₁₀ Melt [23]	Multilayer		Monolayer		Submonolayer	
			Au(1 1 1) (this work)	Cu(1 1 1) ^a [4]	Au(1 1 1) (this work)	Cu(1 1 1) ^a [4]	Au(1 1 1) (this work) ^b	Au(1 1 1) (this work) ^c
b _{1u}	γCH	974						
	γCH	904	904					
	γCH, γCC	724	734	735	731	720	741	738
	γCH, γCC	688	701		694		693	
	γCH, γCC	430				430		
b _{2u}	νCH	3096		3095				
	νCH	3047	3034					
	νCH, βCCH	1580	1571	1625				
	βCCH	1440	1430					
	βCCH	1326	1347	1320				
	βCCH	1280						
	βCCH	1170	1172					
	βCCC	1080	1078					
b _{3u}	νCH	3069	3059					
	νCH	3010						
	νCH, βCCH	1600						
	βCCH	1492	1483	1500				
	βCCH	1190		1195				
	νCC, βCCH	1050	1044					
	γCCC	1016						
	νCC, γCCH	990		980				

v: stretch; β: in-plane-bend; γ: out-of-plane bend; χ: nonplanar twisting.

^a HREELS data.

^b Submonolayer of biphenyl formed after iodobenzene adsorption on rough Au(1 1 1) surface and heating to 300 K.

^c Submonolayer of biphenyl formed after iodobenzene adsorption on Au(1 1 1) surface and heating to 300 K.

identical to those of the surface species formed after iodobenzene reactions induced by heating to 300 K. This comparison is summarized in Table 2. Identification of adsorbed biphenyl products from C₆H₅I decomposition is easier in the IRAS spectra from a roughened surface because more biphenyl is formed on the more reactive, roughened surfaces.

Iodobenzene decomposition occurs at 200–250 K on a roughened surface and 250–300 K on high-quality, well-ordered Au(1 1 1) surfaces. This is consistent with observations that C₆H₅I dissociates on Cu(1 1 1) at 175 K and linear alkyl iodides dissociate at ~80 K higher temperatures on Au(1 1 1) than on Cu(1 1 1). Also, we showed in EID studies that adsorbed phenyl groups on Au(1 1 1) are stable only up to 165 K [12]. Phenyl groups undergo coupling to form biphenyl at higher substrate temperatures. Phenyl coupling

reactions occur at lower temperatures than C–I bond dissociation in adsorbed C₆H₅I on Au(1 1 1). This explains why no phenyl groups were isolated as stable “intermediates” bonded to the surface in “warm-up” studies using IRAS to detect nascent phenyl group formation. Biphenyl is formed immediately on the surface as soon as C–I bond dissociation takes place, and so C₆H₅I cannot be used as a convenient precursor to produce phenyl groups on Au(1 1 1) by thermal processing in UHV.

Regarding possible mechanisms of biphenyl formation, we first refer to previous studies of iodobenzene dissociation Cu(1 1 1) in which Xi and Bent distinguished two mechanisms for biphenyl formation [5]. They found that iodobenzene molecules at low coverage dissociate at 175 K, forming adsorbed phenyl groups that couple at high temperatures of 300–400 K. At higher iodo-

benzene coverages, phenyl groups reacted directly with iodobenzene molecules in a low temperature mechanism to form biphenyl below 210 K. We report here that biphenyl is formed by iodobenzene dissociation Au(1 1 1) at 200–250 K. In other work using EID to generate phenyl groups from benzene films at 90 K, we showed that biphenyl formation occurs at 165 K [12]. Obviously, this low temperature coupling reaction occurs in the absence of coadsorbed iodobenzene. Thus, while we cannot exclude the possibility of a direct reaction between phenyl groups and iodobenzene in the results reported here, such an interaction is not necessary and we propose that biphenyl forms upon C–I bond dissociation at 200–250 K as a result of phenyl group coupling on Au(1 1 1).

4. Conclusions

Iodobenzene (C_6H_5I) chemisorbs on the Au(1 1 1) surface and is partially irreversibly adsorbed. Three molecular desorption peaks of C_6H_5I occur at 290–308, 212 and 188 K, corresponding to desorption of iodobenzene from the monolayer, second layer and multilayer, respectively. The saturation coverage of C_6H_5I in the adsorbed monolayer on Au(1 1 1) at 90 K was estimated to be 0.16 ML.

At monolayer coverage and below, C_6H_5I molecules are oriented with their π -rings parallel to the surface plane. Up to 0.027 ML, or 17%, of the monolayer partially decomposed at 200–250 K to form coadsorbed iodine and biphenyl. Both of these products are strongly chemisorbed, and biphenyl molecules desorb from the surface at 400 K via a desorption rate-limited process. Iodine desorbs from the surface at 750 K.

Iodobenzene thermal decomposition occurs at 200–250 K, which is above the temperature range of 165–180 K where coadsorbed phenyl groups on Au(1 1 1) undergo C–C coupling and form biphenyl. As a result, thermal decomposition of C_6H_5I

cannot be used to produce adsorbed phenyl species on Au(1 1 1) surfaces.

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