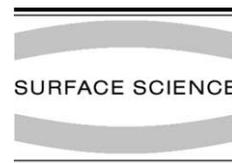




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# IRAS studies of the orientation of acetone molecules in monolayer and multilayer films on Au(1 1 1) surfaces

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## Abstract

We have investigated the interaction of acetone with a Au(1 1 1) surface by use of temperature programmed desorption (TPD) and infrared reflection–absorption spectroscopy (IRAS). We find that acetone reversibly adsorbs on Au(1 1 1), with thermal desorption peaks at 160, 137 and 132 K corresponding to acetone desorption from the monolayer, second layer and multilayer, respectively. IRAS data is used to establish that chemisorbed acetone molecules bind to the Au(1 1 1) surface through the oxygen atom in a  $\eta^1$ -(O) configuration with the molecular plane tilted with respect to the surface plane to give  $C_1$  symmetry at submonolayer and monolayer coverage. In multilayer films, acetone molecules adopt a highly ordered orientation with the molecular plane perpendicular to the metal surface and the C=O bond nearly parallel to the surface plane to give  $C_s$  symmetry. © 2001 Elsevier Science B.V. All rights reserved.

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

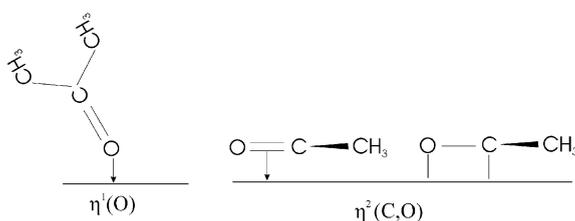
## 1. Introduction

Acetone adsorption on single crystal metal surfaces has been discussed in the literature several times. Avery et al. studied acetone adsorption on Pt(1 1 1) by means of temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS) [1,2]. They established that acetone molecularly adsorbs on Pt(1 1 1) at low temperatures and binds to the surface in both  $\eta^1$ (O) “end-on” and  $\eta^2$ (C,O) “side-on” configurations as shown in Scheme 1.

A majority of acetone molecules adopt the  $\eta^1$ (O) configuration, with the Pt–O–C axis bent in the plane of the molecule, and desorb reversibly at 185 K. Species with a  $\eta^2$ (C,O) bonding geometry have a higher desorption temperature and partially decompose below 220 K. Later, Vannice et al. reproduced and extended these results using TPD, HREELS and infrared reflection–absorption spectroscopy (IRAS) [3]. They found that acetone molecules adsorbed with an  $\eta^2$ (C,O) configuration desorb at 199 K with no decomposition. Unlike the chemistry on Pt(1 1 1), a majority of acetone molecules bind to the Ru(0 0 1) surface in a “side-on”  $\eta^2$ (C,O) configuration and decompose upon heating to form residual carbon, CO<sub>(a)</sub> and H<sub>(a)</sub> [2,4]. Part of the adsorbed acetone is also present as  $\eta^1$ (O) species and these desorb reversibly. On

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Scheme 1.

Pd(1 1 1), surface-bound acetone forms both  $\eta^1(\text{O})$  and  $\eta^2(\text{C},\text{O})$  species.  $\eta^1(\text{O})$ -bonded species desorb molecularly at 200 K or convert into  $\eta^2(\text{C},\text{O})$  species which partially decompose or desorb at higher temperatures [5]. Sexton and Hughes reported that acetone molecularly and reversibly adsorbed on the Cu(1 0 0) surface in a  $\eta^1(\text{O})$  configuration. Acetone in the monolayer desorbed at 170 K [6]. Lamont et al. showed that acetaldehyde adsorbs molecularly on Cu(1 1 1) at 110 K in a  $\eta^1(\text{O})$  configuration as well [7]. Prabhakaran and Rao later suggested that there was partial acetone decomposition on Cu(1 1 0) below 180 K [8] based on HREELS data.

The nature of the acetone–metal chemisorption bond has been described by electron donation from the oxygen lone-pair orbitals to unfilled metal orbitals for the case of a  $\eta^1(\text{O})$  binding geometry, and electron donation from carbonyl  $\pi$ -orbitals to unfilled metal orbitals along with electron back donation of metal electrons to carbonyl  $\pi^*$ -orbitals in the case of  $\eta^2(\text{C},\text{O})$  orientations [5,9]. Analogous inorganic cluster compounds containing acetone ligands and a wide variety of metal centers are well known [10–16] and mechanisms of ketone coordination to a metal center have been discussed [4,17].

In the course of our studies of hydrocarbon oxidation on gold surfaces, we have found it is important to have vibrational fingerprints for oxygen-containing molecules adsorbed on gold surfaces. It is for this reason that we undertook this study. In addition, further investigations of the adsorption geometry and reactivity of acetone on metal surfaces increase our understanding of metal catalysis and also compliment studies of aldehydes and ketones on gold and other metal surfaces.

Briefly, we found that acetone adsorbs reversibly on Au(1 1 1), with desorption peaks at 160, 137 and 132 K corresponding to acetone desorption from the monolayer, second layer and multilayer, respectively. IRAS data suggest that at both submonolayer and monolayer coverage, acetone molecules bind to the Au(1 1 1) surface in a  $\eta^1(\text{O})$  configuration with  $C_1$  symmetry, where the molecular plane is tilted with respect to the surface plane. Acetone molecules condense in multilayer films in a highly ordered orientation with  $C_s$  symmetry in which the molecular plane is oriented perpendicular to the surface and the C=O bond is only tilted slightly with respect to the surface plane.

## 2. Experimental methods

These experiments were performed in a stainless steel UHV chamber equipped for Auger electron spectroscopy (AES), low energy electron diffraction (LEED), temperature programmed desorption (TPD) and Fourier-transform infrared (FTIR) spectroscopy studies. The system had a base pressure of  $2 \times 10^{-10}$  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<sup>+</sup> ion sputtering (0.5 keV,  $P_{\text{Ar}} = 6 \times 10^{-5}$  Torr,  $I_{\text{sample}} = 1.5 \mu\text{A}$ ) 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 [18]. No surface carbon was detected by AES.

Acetone ( $\text{C}_3\text{H}_6\text{O}$ ) (Mallinckrodt, 99.8+%) was degassed before dosing by several freeze–pump–thaw cycles that were carried out using the gas-handling line attached to the UHV chamber. Acetone was introduced into the 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 K/s was used.

IRAS was carried out at a grazing incidence angle of  $86^\circ$  from the surface normal. An Infinity<sup>®</sup> 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  $4\text{ cm}^{-1}$  and by averaging 1000 scans taken over 5 min. All of the spectra reported were taken with the sample at a temperature of 87–90 K and ratioed against the clean surface spectrum as a background.

The IR spectra of liquid acetone (trapped between two KBr disks) was obtained with the same spectrometer described above, but using a wide-band, liquid-nitrogen cooled, MCT detector. These spectra were taken in the transmission mode at a spectrometer resolution of  $1\text{ cm}^{-1}$  by averaging 10 scans over 50 s.

Acetone coverages are reported with respect to saturation of the chemisorbed monolayer ( $\theta = 1\text{ ML}$ ) as determined in TPD experiments.

### 3. Results

Acetone was the only desorption product detected in TPD experiments after acetone exposures on the Au(111) surface at 90 K. We monitored acetone evolution by using the signal at 43 amu which corresponds to the most intense signal in the mass spectrum of gas-phase acetone. As shown in Fig. 1, adsorbed acetone on Au(111) exhibited three desorption states at 160, 137 and 132 K that we assign to desorption from the monolayer, second layer and multilayer, respectively. At small coverages of  $\sim 0.05\text{ ML}$  of chemisorbed acetone, the desorption peak temperature shifts to 166 K.

Using Redhead analysis, and assuming first-order desorption kinetics with a pre-exponential factor of  $10^{13}\text{ s}^{-1}$ , the acetone desorption activation energy ( $E_d$ ) can be estimated to be 9.9 and 8.3 kcal/mol for the first ( $T_d = 160\text{ K}$ ) and second ( $T_d = 137\text{ K}$ ) adsorbed layers, respectively. Lead-

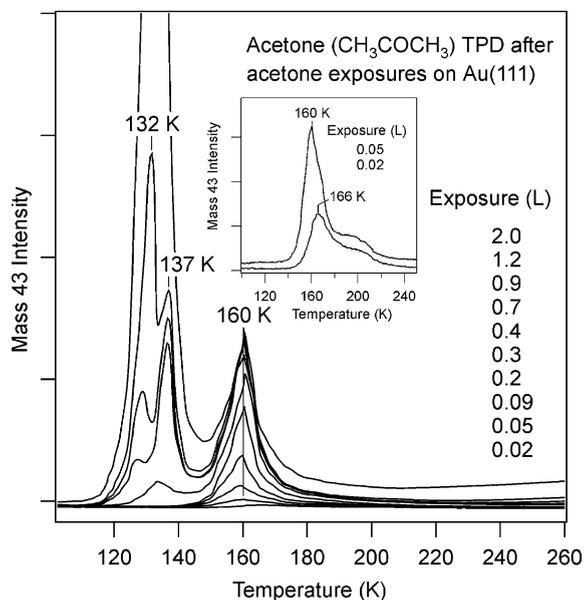


Fig. 1.  $\text{C}_3\text{H}_6\text{O}$  TPD spectra after  $\text{C}_3\text{H}_6\text{O}$  exposures on Au(111) at 90 K.

ing edge analysis of the zero-order multilayer desorption peak yielded a desorption activation energy of 7.3 kcal/mol which is consistent with the acetone enthalpy of vaporization 7.4 kcal/mol [19]. Because there is not usually any appreciable barrier to weak, molecular adsorption, these values for  $E_d$  are good estimates of the respective adsorption energies on Au(111) surfaces.

IR spectra show that acetone adsorbed molecularly on Au(111) at 90 K. These spectra are shown for low coverages and thick films in Figs. 2 and 3, respectively, along with expanded  $\nu(\text{CO})$  and  $\nu(\text{CH}_3)$  regions of the spectra in Fig. 4. Only four vibrational bands at 1669, 1437, 1364 and  $1091\text{ cm}^{-1}$  were observed at a coverage of 0.25 ML. At 0.5-ML acetone coverage, two new bands at 1695 and  $2943\text{ cm}^{-1}$  appear in the spectra, as shown in Fig. 2. Acetone present at 1-ML coverage is characterized by the disappearance of the band at  $1669\text{ cm}^{-1}$  and the appearance of a band at  $1236\text{ cm}^{-1}$ . As shown in Fig. 3, new vibrational bands at 538, 902, 1702, 1716, 2968 and  $3001\text{ cm}^{-1}$  appear in the spectra at coverages exceeding 1 ML, and then the frequencies shift only by small amounts with increasingly thick films.

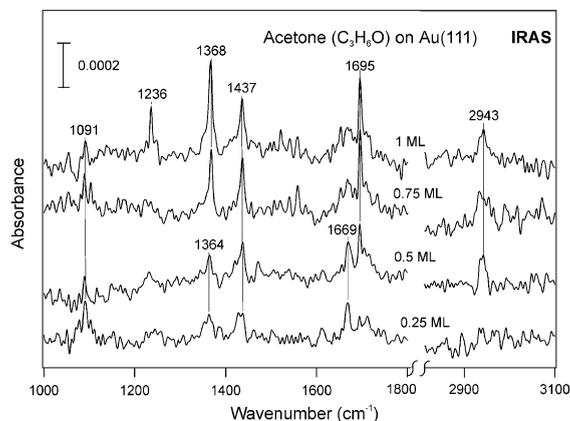


Fig. 2. IRAS spectra for  $C_3H_6O$  adlayers at coverages of 0.25–1 ML on Au(1 1 1) at 90 K.

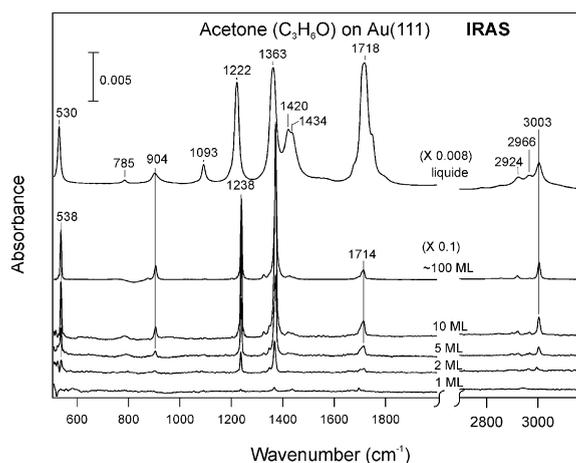


Fig. 3. IRAS spectra for  $C_3H_6O$  adlayers at coverages of 1–100 ML on Au(1 1 1) at 90 K. The IR spectrum of liquid-phase  $C_6H_5NO_2$  is also provided for comparison.

#### 4. Discussion

Aldehydes and ketones bound to metal surfaces in a  $\eta^2(C,O)$  configuration form a stronger chemisorption bond with the surface and desorb at higher temperatures than those that coordinate in a  $\eta^1(O)$  fashion. Usually  $\eta^1(O)$ -bonded species desorb prior to decomposition and  $\eta^2(C,O)$ -coordinated species decompose before the chemisorption bond is broken and desorption occurs [5]. We had expected that acetone would coordinate

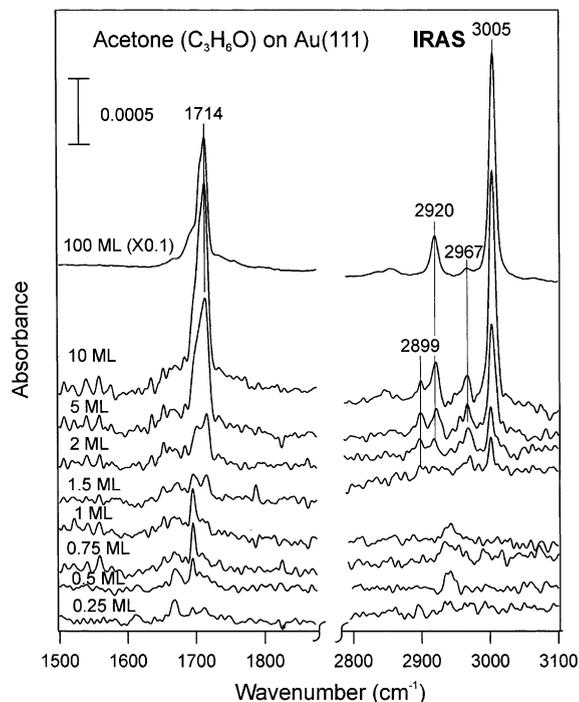


Fig. 4. Expanded plots of the  $\nu(CO)$  and  $\nu(CH_3)$  regions of the IRAS spectra for  $C_3H_6O$  adlayers at coverages of 0.25–10 ML on Au(1 1 1) at 90 K.

weakly in a  $\eta^1(O)$  geometry to the relatively unreactive Au(1 1 1) surface, just as other aldehydes and ketones are known to coordinate to other metal surfaces.

FTIR data confirms this expectation and furthermore determines the molecular orientation adopted by acetone bonded in this manner. TPD experiments show only a weakly bound chemisorbed state of acetone with a desorption temperature of 160 K (just 23 K higher than the desorption temperature of the condensed-phase, acetone multilayer) consistent also with this expectation. Our results on Au(1 1 1) are consistent with the values of  $T_d = 170$  K reported by Sexton and Hughes for acetone weakly adsorbed on Cu(1 0 0) [6] and indicate much weaker bonding on Au(1 1 1) and Cu(1 0 0) than on Pd(1 1 1), Pt(1 1 1) and Ru(0 0 1) [2–5].

In order to determine the molecular orientation of acetone on the surface, we first considered that acetone molecules belong to the symmetry group

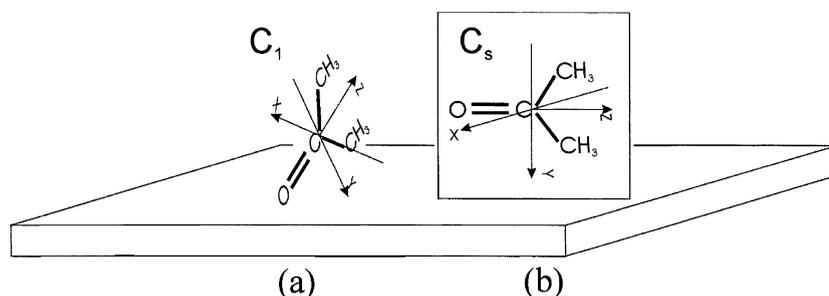


Fig. 5. Selected orientations of acetone molecules bonded in a  $\eta^1(\text{O})$  "end-on" configuration on Au(111) surfaces: (a) with all molecular axes tilted with respect to the surface plane to give  $C_1$  symmetry, and (b) with the molecular plane perpendicular to the surface plane and the (C=O) double bond (molecular Z axis) almost parallel to the surface to give  $C_s$  symmetry.

$C_{2v}$ . There are 24 normal vibrational modes that are classified into the following symmetry types:  $\Gamma_v = 8A_1 + 4A_2 + 7B_2 + 5B_1$ . These modes may be divided into motions with dynamic dipoles "in-plane" ( $A_1$  and  $B_2$ ) and "out-of-plane" ( $A_2$  and  $B_1$ ) with respect to the planar acetone-molecule  $(\text{CH}_3)_2\text{CO}$  skeleton. Dynamic dipole moments of the  $A_1$ ,  $B_1$  and  $B_2$  modes occur along the Z, X and Y molecular axes, respectively. This is illustrated in Fig. 5(b). Vibrational mode assignments for adsorbed acetone molecules have been made based on comparisons to the IR spectra of liquid-phase and gas-phase acetone [20,21] and previous vibrational assignments for acetone chemisorbed on Pt(111), Ru(001) and Pd(111) [1,2,5].

At 0.25-ML coverage, only four vibrational bands are present in the spectra:  $1091\text{ cm}^{-1}$  ( $\rho\text{CH}_3$ ,  $B_1$ ),  $1364\text{ cm}^{-1}$  ( $\delta_s(\text{CH}_3)$ ,  $B_2$ ),  $1437\text{ cm}^{-1}$  ( $\delta_{\text{as}}(\text{CH}_3)$ ,  $A_1$ ) and  $1669\text{ cm}^{-1}$  ( $\nu(\text{C}=\text{O})$ ,  $A_1$ ). At higher coverages, a band at  $2936\text{ cm}^{-1}$  ( $\nu\text{CH}$ ,  $B_2$ ) and one more band corresponding to C=O stretching at  $1695\text{ cm}^{-1}$  ( $\nu(\text{C}=\text{O})$ ,  $A_1$ ) appear in the spectrum. At 1 ML, a new mode at  $1236\text{ cm}^{-1}$  ( $\nu_{\text{as}}\text{CCC}$ ,  $B_2$ ) appears in the spectra. With increasing acetone coverage, new modes at  $538\text{ cm}^{-1}$  due to CCO bending ( $\beta\text{CCO}$ ,  $B_2$ ) and  $904\text{ cm}^{-1}$  from  $\text{CH}_3$  rocking ( $\rho\text{CH}_3$ ,  $B_2$ ) were detected. The appearance of the  $\beta(\text{CCO})$  band at  $530\text{ cm}^{-1}$  and the  $\rho(\text{CH}_3)$  band at  $904\text{ cm}^{-1}$  is associated simply with an increase in the absorption intensity because of the increasing acetone coverage rather than with a significant change in the molecular orientation. The  $\beta(\text{CCO})$  frequency is near the edge of the cut-

off region for the MCT detector and thus it can be detected only when it has significant intensity. At 2-ML coverage, the  $\nu(\text{CO})$  peak splits into two bands at  $1702$  and  $1716\text{ cm}^{-1}$  corresponding to species present in the acetone monolayer and multilayer, respectively. In the CH stretching region, the band at  $2943\text{ cm}^{-1}$  disappears at 2 ML, and four new modes at  $2898$  ( $\nu\text{CH}$ ,  $A_1$ ),  $2918$  ( $\nu\text{CH}$ ,  $A_1$ ),  $2968$  ( $\nu\text{CH}$ ,  $B_1$ ) and  $3001\text{ cm}^{-1}$  ( $\nu\text{CH}$ ,  $B_2$ ) were detected in the spectrum.

The bonding geometry of adsorbed acetone as probed by vibrational spectra was thoroughly investigated and analyzed on Pt(111) and Ru(001) surfaces [1,2,4]. It was found that  $\nu(\text{CO})$  was significantly red-shifted from the liquid-phase value of  $1710\text{ cm}^{-1}$  to the range of  $\nu(\text{CO})$  in organometallic complexes, e.g.,  $\{[(\text{CH}_3)_2\text{CO}]_6\text{M}\}^{2+}$  has  $\nu(\text{CO}) = 1650\text{--}1670\text{ cm}^{-1}$  [4,10] for the  $\eta^1(\text{O})$  bonding configuration. This shift was associated with a weakening of the C=O bond. On the other hand, the vibrational frequencies of the modes in the rest of molecule were nearly unperturbed, with the exception of a small blue shift observed for  $\beta(\text{CCO})$ ,  $\nu_{19}$  and  $\nu_{\text{as}}(\text{CCC})$ ,  $\nu_{17}$ . The vibrational fingerprint of acetone adsorbed on Au(111) at submonolayer coverages is very similar to that of acetone in a  $\eta^1(\text{O})$  coordination on Pt(111), Pd(111) and Ru(001). This comparison is provided in Table 1. For example, the red-shifted  $\nu(\text{CO})$  band at  $1669\text{ cm}^{-1}$  on Au(111) is very close to  $\nu(\text{CO})$  of acetone on Ru(001) and  $\eta^1$ -acetone complexes of Ru ( $1661$  and  $1665\text{ cm}^{-1}$  [10,11,13]). The frequencies of the other bands detected at

Table 1  
Vibrational frequencies ( $\text{cm}^{-1}$ ) and mode assignments for IR spectra of acetone ( $\text{C}_3\text{H}_6\text{O}$ )

Symmetry	No.	Type of mode <sup>a</sup>	$\text{C}_3\text{H}_6\text{O}$ [21] Liq.	Pt(1 1 1) [1] 1 ML	Pd(1 1 1) [5] 1 ML	Ru(0 0 1) [4] 1 ML	Au(1 1 1) [this work]					
							1/4 ML	1 ML	2 ML	10 ML	100 ML	
$A_1$	1	$\nu\text{CH}$							2898	2899		
	2	$\nu\text{CH}$	2924						2918	2921	2920	
	3	$\nu\text{C=O}$	1710						1716	1714	1714	
					1630	1670	1650	1669	1695	1702		
	4	$\delta_{\text{as}}(\text{CH}_3)$	1434	1430	1425			1437	1437			
	5	$\delta_{\text{s}}(\text{CH}_3)$	(1364)									
	6	$\beta(\text{CH}_3)$	1091		1065							
	7	$\nu_{\text{s}}\text{CCC}$	785.5		805	780–825						
	8	$\gamma\text{CCC}$	(399)									
$A_2$	9	$\nu\text{CH}$										
	10	$\delta(\text{CH}_3)$										
	11	$\beta\text{CCC}$										
	12	$\chi\text{CH}_3$										
$B_2$	13	$\nu\text{CH}$	3004	3000						3001	3003	3005
	14	$\nu\text{CH}$	2937						2943			
	15	$\delta_{\text{as}}(\text{CH}_3)$	1418									
	16	$\delta_{\text{s}}(\text{CH}_3)$	1361	1350	1360	1395–1440	1364	1368	1368	1372	1372	
	17	$\nu_{\text{as}}\text{CCC}$	1220.5	1245	1245				1236	1237	1238	1238
	18	$\rho\text{CH}_3$	902	910						902	905	905
	19	$\beta\text{CCO}$	530	575		515–540				538	538	538
$B_1$	20	$\nu\text{CH}$	2964		2960	2950–2995				2968	2967	2967
	21	$\delta(\text{CH}_3)$										
	22	$\rho\text{CH}_3$	1091.5	1080		1050–1110	1091	1091	1084	1095	1097	
	23	$\gamma\text{C=O}$	(483)									
	24	$\chi\text{CH}_3$	(109)									

<sup>a</sup>  $\nu$ , stretch;  $\delta$ , deformation;  $\rho$ , rocking;  $\beta$ , in-plane bend;  $\gamma$ , out-of-plane bend;  $\chi$ , nonplanar twisting. Gas phase values are shown in parenthesis (Ref. [21]).

submonolayer and monolayer coverages are almost identical to those found in the liquid phase. Thus, we conclude that acetone binds weakly to the Au(1 1 1) surface through its oxygen atom in a  $\eta^1(\text{O})$  configuration. At 0.5 ML coverage,  $\nu(\text{CO})$  splits into two modes at 1669 and 1695  $\text{cm}^{-1}$ , and we associate this to formation of an acetone adsorption state with a slightly different adsorption geometry or bonded at a different site.

According to the surface selection rule [22], dynamic dipoles parallel to the metal surface are very strongly screened such that those modes are not observed in the IR spectrum. At submonolayer and monolayer coverages, vibrational modes that have  $A_1$ ,  $B_1$  and  $B_2$  symmetry are all detected in the spectrum, and the relative absorption intensities of these modes are very similar to those in liquid

phase. That means that none of the molecular symmetry axes is parallel to the surface plane, i.e., the molecular plane is tilted with respect to the surface plane. Thus, we conclude that acetone molecules bind to the surface in a  $\eta^1(\text{O})$  configuration through its oxygen atom, with the molecular plane tilted with respect to the surface to give  $C_1$  symmetry as shown in Fig. 5(a). The vibrational spectrum of adsorbed acetone does not change appreciably over the range of submonolayer to monolayer coverage. We associate the appearance of new bands in the CH stretching region simply with an increase in intensity above the noise rather than a change in molecular orientation.

However, at coverages exceeding 1 ML, the relative intensity of the  $\nu(\text{CO})$  ( $\nu_3$ ,  $A_1$ ) band dra-

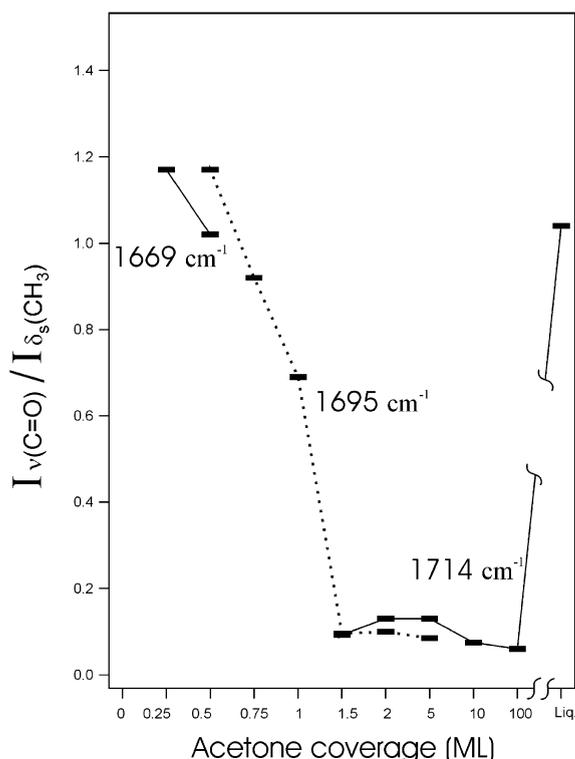


Fig. 6. Relative absorption intensity in IRAS of the  $\nu_3$ ,  $\nu(\text{CO})$ ,  $A_1$  band with respect to the  $\nu_{16}$ ,  $\delta_s(\text{CH}_3)$ ,  $B_2$  band in adsorbed acetone films on Au(111) at 90 K.

matically decreases with respect to the band from  $\delta_s(\text{CH}_3)$  ( $\nu_{16}$ ,  $B_2$ ) as shown in Fig. 6. This is clear evidence of a change in the acetone orientation in the adlayer such that the  $\nu(\text{CO})$  mode is screened by the surface to a much greater extent than a mode with  $B_2$  symmetry. At the same time, the band at  $1091\text{ cm}^{-1}$  ( $\nu_{22}$ ,  $\rho\text{CH}_3$ ,  $B_1$ ) practically disappears from the spectra. Its relative intensity in the 10-ML film to that of the band at  $1238\text{ cm}^{-1}$  ( $\nu_{17}$ ,  $\nu_{\text{as}}(\text{CCC})$ ,  $B_2$ ) is only 1%. This means that acetone molecules are oriented with the molecular  $X$  axis parallel to the Au(111) surface plane. Thus, acetone molecules in these condensed, multilayer films are oriented with the molecular plane perpendicular to the metal surface with the  $\text{C}=\text{O}$  double bond nearly parallel to the surface as shown in Fig. 4(b). This orientation of acetone molecules in these multilayer thin films is identical to that reported for crystalline acetone [23–25].

## 5. Conclusion

Acetone reversibly adsorbs on Au(111) surfaces at low temperatures under UHV conditions. Three desorption peaks in TPD occur at 160, 137 and 132 K corresponding to desorption from the chemisorbed monolayer, second layer and multilayer, respectively. In the chemisorbed monolayer, acetone is coordinated to the Au surface through the oxygen atom in a  $\eta^1(\text{O})$  configuration. The chemisorbed molecule adopts an orientation with  $C_1$  symmetry in which the molecular plane is tilted with respect to the metal surface plane. The  $\text{C}=\text{O}$  stretching frequency is red-shifted and occurs at 1669 and  $1695\text{ cm}^{-1}$  for 0.25 and 1-ML coverages, respectively. In condensed, physisorbed multilayer films, acetone molecules are highly oriented with the molecular plane perpendicular to the surface and the  $\text{C}=\text{O}$  double bond nearly parallel to the Au(111) surface plane to give  $C_s$  symmetry.

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