



Adsorption of benzene on the five-fold surface of the i-Al70Pd21Mn9 quasicrystal

Journal:	<i>Philosophical Magazine & Philosophical Magazine Letters</i>
Manuscript ID:	TPHM-05-May-0217.R1
Journal Selection:	Philosophical Magazine
Date Submitted by the Author:	05-Jul-2005
Complete List of Authors:	Hoelt, Jon; The University of Liverpool, Surface Science Ledieu, Julian; The University of Liverpool, Surface Science Haq, Sam; The University of Liverpool, Surface Science Lograsso, Thomas; Iowa State University, Ames Laboratory Ross, Amy; Ames Laboratory, Department of Materials Science and Engineering McGrath, Ronan; The University of Liverpool, Physics
Keywords:	surfaces, SPM, scanning probe microscopy, quasicrystals, quasicrystalline alloys
Keywords (user supplied):	benzene



1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Adsorption of benzene on the five-fold Surface of the
***i*-Al₇₀Pd₂₁Mn₉ quasicrystal**

J.T. Hoefft*, J. Ledieu†, S. Haq

*Surface Science Research Centre,
The University of Liverpool,
Liverpool L69 3BX, UK*

T.A. Lograsso, A.R. Ross

*Ames Laboratory, Iowa State University,
Ames, IA 50011, US*

R. McGrath‡

*Department of Physics and Surface Science Research Centre,
The University of Liverpool,
Liverpool L69 3BX, UK*

(Dated: July 5, 2005)

* Present Address: Universität Hamburg, Institut für Experimentalphysik, Luruper Chaussee 149, D-22761 Hamburg, Germany

† Present Address: LSG2M, CNRS UMR 7584, Ecole des Mines, Parc de Saurupt, 54042 Nancy Cedex, France

‡ Corresponding author

Abstract

The adsorption behaviour of benzene (C_6H_6) on the five-fold surface of the icosahedral $Al_{70}Pd_{21}Mn_9$ quasicrystal has been investigated. Reflection absorption infrared spectroscopy (RAIRS) data taken at a temperature of 92 K indicate molecular adsorption. The adsorption geometry of the molecules is found to change from parallel to the surface to oblique geometries as the dose is increased from **monolayer to multilayer coverages**. Scanning tunnelling microscopy (STM) images show that the molecules adsorb in a disordered fashion. The adsorbate layer is found to completely desorb at 153 K leaving the substrate unchanged.

PACS numbers: 61.44.Br, 68.35.Bs, 68.37.Ef

I. INTRODUCTION

Quasicrystals are metallic alloys which possess long-range order but yet are not periodic in some or all spatial dimensions. The surfaces of quasicrystals have been the subject of intense scrutiny for a number of years, and a consensus has emerged that certain clean quasicrystal surfaces prepared under ultra high vacuum conditions are unreconstructed terminations of the bulk structure^{1,2}. In (scanning tunnelling microscopy) STM measurements, these surfaces are characterised by a few local structural motifs that are visible all over the surface but without periodicity. Thus these surfaces can serve as substrates for investigating the interaction of adsorbates with a quasiperiodic surface.

There has been great interest recently in observing and understanding the growth of solids on quasicrystal surface templates, where many new and unexpected growth phenomena have been observed³. The possibility that films prepared on quasicrystalline surfaces could exhibit novel electronic and magnetic properties provides a compelling motivation for such studies. The adsorption of molecular species is also of interest in achieving an understanding of the surface reactivity of quasicrystals, and to compare molecular adsorption behaviour with the extensive literature for molecular adsorption on single crystal surfaces. The possibility of using adsorbed molecules to modify or functionalise surfaces, in particular for technologically relevant applications such as reducing friction coefficients⁴, provides an added motivation.

Despite this, there have been comparatively few studies of molecular adsorption on quasicrystals. Thiel and co-workers have investigated oxygen and water adsorption, with a view to understanding the oxidation behaviour of quasicrystal surfaces and related approximants⁵⁻¹². Here dissociative adsorption takes place, and the adsorbed species react aggressively with the substrate destroying the surface order. A similar picture was found for H₂S adsorption¹³. Jenks *et al.* found using temperature programmed reaction spectroscopy that methanol, iodoethane and 1-iodopropane dissociatively adsorb on *i*-AlPdMn, with a variety of species being evolved¹².

Besides affecting reactivity and surface functionality, if molecules were found to adsorb in unique adsorption sites, then it should be possible to observe a two-dimensional quasiperiodic molecular array. Ledieu *et al.*¹⁴ investigated the adsorption of C₆₀ on *i*-AlPdMn, where it was found that the fullerene molecules adsorb intact and preferentially dock in the pentagonal hollow sites (the truncated Bergman clusters)¹⁵ at low coverages. Thus they exhibit

1
2
3 local order with τ -scaling of the inter-molecular distances. This study suggests that they
4 may be a geometric factor in the preferred adsorption site: C_{60} molecules have pentagonal
5 rings of C atoms. However it was impossible to determine the exact configuration of the
6 molecules with relation to the substrate in that study.
7
8
9

10 In a follow-up to that work, a survey was undertaken using reflection adsorption infrared
11 spectroscopy (RAIRS) of the adsorption of several other molecules¹⁶. In that study, benzene
12 was found to be a promising candidate for ordered molecular adsorption on i -Al₇₀Pd₂₁Mn₉
13 at low temperatures, as the substrate low energy electron diffraction (LEED) pattern was
14 found to be unaffected by the adsorption of the aromatic molecules. The distinctive planar
15 hexagonal geometry of the C_6H_6 molecule poses the interesting question of whether this
16 six-fold molecular symmetry leads to a six-fold symmetry of the overlayer or if the substrate
17 influence is strong enough to establish an adsorbate structure governed by five-fold symme-
18 try. Here we report in more detail on our investigations of this system carried out using
19 reflection absorption infrared spectroscopy (RAIRS) and STM.
20
21
22
23
24
25
26
27
28
29

30 II. EXPERIMENTAL DETAILS

31
32
33 Before insertion into ultra high vacuum (UHV) the sample was polished according to
34 an established procedure described elsewhere.^{17,18} Cleaning the crystal *in situ* was done by
35 cycles of Ar⁺ ion bombardment for 45 minutes at 3 keV followed by annealing to 970 K
36 for about 1-2 h by e-beam heating. The LEED pattern after this procedure indicated good
37 quasicrystalline order over an energy range from 12-246 eV.
38
39
40
41

42 For the RAIRS studies the sample was mounted in a purpose-built UHV chamber
43 equipped with LEED and a quadrupole mass spectrometer. Using a K-type thermocou-
44 ple attached under the tantalum straps holding the sample the temperature reading had
45 an estimated accuracy of ± 10 K. The spectrometer employed was a Galaxy series FT-IR
46 of Mattson Instruments. Spectra consisted of averages of 200 scans and were recorded at
47 4 cm⁻¹ resolution.
48
49
50
51
52

53 STM images were recorded in a separate chamber using an Omicron variable temperature
54 STM operated with a liquid helium flow cryostat to achieve sample temperatures of 21 K.
55 For temperature measurement a Si diode mounted on the cooling block clamped to the
56 sample served as the closest measuring point. A heating system in the flow cryostat allowed
57
58
59
60

1
2
3 intermediate temperatures to be achieved. The system was also equipped with an Omicron
4 LEED/Auger system.
5

6
7 Benzene was degassed by numerous freeze–thaw cycles before dosing. Dosing of benzene
8 took place by maintaining a background pressure of 1×10^{-9} mbar controlled via a leak
9 valve in the analysing chamber. A quadrupole mass spectrometer was employed to monitor
10 the purity of the benzene. It was also used to determine the desorption temperature of the
11 adsorbed molecules.
12
13
14
15

16 17 18 III. RESULTS AND DISCUSSION 19

20
21 The infra-red reflectivity was recorded during adsorption of benzene at low temperatures
22 (see Fig. 1). To identify the bands observed they were compared with the position of bands
23 observed for molecular benzene adsorbed on a Cu(110) surface¹⁹. Spectra taken at 92 K
24 (Fig. 1(a) and (b)) with small doses of benzene exhibit a single band around $677\text{-}679\text{ cm}^{-1}$
25 which is attributed to an out-of-plane C-H bending mode, $\gamma\text{CH}(\nu_4)$. Due to the dipole
26 selection rules this mode is the only one active in an adsorption geometry with the ring
27 parallel to the surface. Since this band is the only significant feature observed, we conclude
28 that molecular adsorption occurs flat on the surface at these low doses.
29
30
31
32
33

34
35 After a larger dose of 28 L (Fig. 1(c)) this band is slightly shifted to $687\text{-}689\text{ cm}^{-1}$ and
36 additional features at 1037 cm^{-1} and 1479 cm^{-1} appear. These peaks are attributed to C-H
37 in-plane bending modes and a C-C stretch mode, which corresponds to the ‘breathing’ mode
38 of the carbon ring. Due to the RAIRS selection rules this mode will only be observable in an
39 adsorption geometry not parallel to the surface¹⁹. We conclude that a non-coplanar stacking
40 of the benzene rings occurs at higher coverages. In annealing the overlayer it was found that
41 desorption was complete at 153 K.
42
43
44
45
46
47

48 Figure 2(a) shows the clean surface imaged at 21 K using STM after the preparation
49 procedure described before. The resolution at this temperature, while adequate to resolve
50 protrusions of atomic dimensions, is not as good as the best obtained on samples similarly
51 prepared and imaged at room temperature. This is due to thermal drift in the system.
52 In particular the truncated Bergman clusters, which are usually imaged as five-fold “dark
53 stars” are not well-resolved¹⁸. However the Fast Fourier Transform (FFT) of this surface
54 region (not shown) displays ring of ten spots as expected for the five-fold symmetric surface
55
56
57
58
59
60

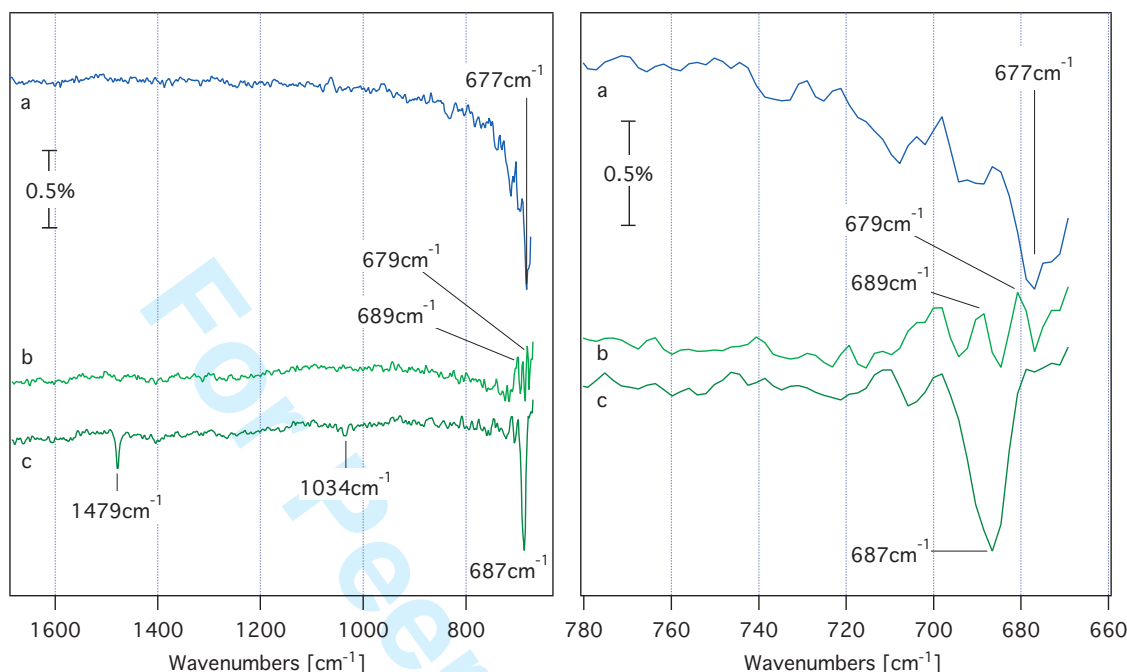
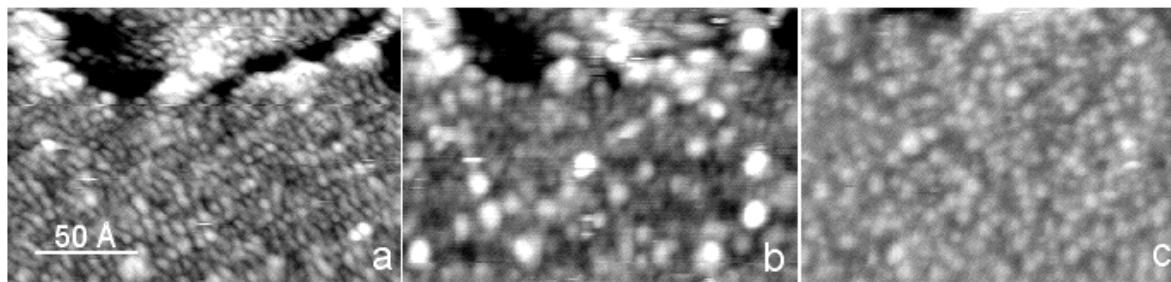


FIG. 1: RAIRS data recorded during adsorption of benzene on the five-fold surface of the $\text{Al}_{70}\text{Pd}_{21}\text{Mn}_9$ quasicrystal. The left-hand panel contains survey scans while the right-hand panel shows a magnified view of the region from $600\text{--}780\text{ cm}^{-1}$. The doses correspond to (a) 1 L (92 K); (b) 6 L (92 K) and (c) 28 L (105 K).

of this quasicrystal.

The surface was exposed to benzene at 21 K while being scanned continuously. Some of the results are shown in Fig. 2(b) and (c). The adsorbed molecules impaired scanning conditions, such that it was not possible unambiguously to relate molecular adsorption sites to positions on the clean surface. Nevertheless at the 0.3 L coverage, isolated protrusions are visible which can be interpreted as corresponding to individual benzene molecules. After a 6 L dose, the surface is completely covered with benzene molecules, and the coverage is of the order of 1 ML. Note that the coverage for the 6 L dose studied using RAIRS will be equal to or less than the coverage after the corresponding dose using the STM because of a possible temperature dependence of the sticking coefficient. Therefore the parallel adsorption geometry observed in the RAIRS experiment corresponds to a monolayer or sub-monolayer

1
2
3 coverage; the change in the adsorption geometry observed in the RAIRS can therefore be
4 associated with the formation of a benzene multilayer.
5
6



17
18 FIG. 2: $200\text{\AA} \times 150\text{\AA}$ images (a) the clean five-fold surface of the AlPdMn quasicrystal (b) Same
19 region of the surface after exposure to 0.3 L of benzene; (c) Surface after exposure to 6 L of benzene.
20 (a) and (b) were taken at a temperature of 21 K, while (c) was at a temperature of 90 K.
21
22
23
24
25

26 The molecules do not appear to display any ordered pattern at any coverage. No diffusion
27 of molecules was observed. After allowing the sample to warm up above the desorption
28 temperature as determined in the RAIRS experiments (153K) the clean surface was found
29 to be restored with no benzene molecules or fragments remaining. FFTs of images of the
30 surface after desorption display rings of 10 spots. The LEED pattern recorded after benzene
31 deposition was comparable in quality to the one recorded beforehand. We can conclude that
32 the benzene molecules desorb entirely leaving the surface unchanged.
33
34
35
36
37
38

39 The results of this work can be compared with the adsorption of benzene molecules **on**
40 **the surfaces of related single crystal metal surfaces.** Benzene adsorbs on Al(111) at 90 K
41 with the ring-plane parallel to the surface²⁰. Furthermore the desorption temperature for
42 the monolayer phase is 150 K, very close to the temperature found in the current study.
43 The bonding was found to be rather weak and ionic in character. In contrast, on Pd(110)
44 benzene does not begin to desorb until a temperature of $\approx 350\text{ K}$ ²¹. Although the molec-
45 ular orientation on Pd(110) was not determined it was found that benzene adsorbs in the
46 rectangular hollow sites characteristic of (110) surfaces to form an ordered $c(4 \times 2)$ overlayer.
47 Overall there are much closer similarities for our study with benzene on Al(111), which is
48 consistent with our understanding that the exposed surface is Al rich¹⁸.
49
50
51
52
53
54
55
56

57 The lack of molecular ordering on the quasicrystal indicates that the interaction with the
58 substrate is not insubstantial; it appears that the molecules either stick where they land
59
60

1
2
3 upon adsorption, or diffuse after adsorption to a preferred location and then stick. If this
4 latter scenario is the case, then the absence of order would imply that different adsorption
5 sites are being occupied. The fact that the clean surface is recovered after desorption at
6 153 K indicates that the interaction with the surface is not chemically aggressive.
7
8

9
10 These results add to the limited database of work on molecular adsorption on quasicrystals
11 in the literature. A consistent picture is emerging. Molecules which adsorb dissociatively
12 appear to interact aggressively and in doing so destroy the quasiperiodic order of the clean
13 surface. Molecules which adsorb intact tend to do so in a way which does not lead to
14 ordered molecular arrays which are found on crystalline surfaces²¹. In terms of transfer of
15 quasicrystallinity from the substrate 'template' to the adsorbed species, it would appear
16 that metallic species hold out the best prospects for ordered growth³.
17
18
19
20
21
22
23
24

25 IV. SUMMARY

26
27
28 The low-temperature adsorption of benzene molecules on the five-fold surface of
29 Al₇₀Pd₂₁Mn₉ has been investigated using RAIRS, LEED and STM. At sub-monolayer cov-
30 erages, RAIRS indicates that the molecules adsorb in a planar geometry, while at higher
31 coverages a transition to a non-planar adsorption geometry takes place. There is no evidence
32 in STM for the formation of an ordered 2-d molecular overlayer. The adsorbed molecules
33 desorb completely upon annealing to 153 K. This behaviour is similar to that of benzene
34 adsorbed on Al(111)²⁰..
35
36
37
38
39
40

41 We acknowledge the UK Engineering and Physical Science Research Council (grant
42 number GR/S19080/01) and the European Union Marie Curie Development Fund (award
43 HPMD-CT-2001-00093) for funding this work.
44
45
46
47
48
49

50 ¹ Progress in Surface Science, edited by P.A. Thiel 75 (2004).

51 ² R. McGrath, J. Ledieu, E. J. Cox, and R. D. Diehl, J. Phys.: Condensed Matter **14**, R119
52 (2002).
53

54 ³ V. Fourne and P. A. Thiel, J. Phys. D: Appl. Phys. **38**, R83 (2004).
55

56 ⁴ W. Allers, C. Hahn, M. Lohndorf, S. Lukas, S. Pan, U.D. Schwarz, and R. Wiesendanger,
57 Nanotechnology **7**:(4), 346 (1996).
58
59
60

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- ⁵ S. L. Chang, W. B. Chin, C. M. Zhang, C. J. Jenks, and P. A. Thiel, *Surf. Sci.* **337**, 135 (1995).
- ⁶ P. J. Pinhero, S. L. Chang, J. W. Andereg, and P. A. Thiel, *Philos. Mag. B-Phys. Condens. Matter Stat. Mech. Electron. Opt. Magn. Prop.* **75**, 271 (1997).
- ⁷ P. J. Pinhero, D. J. Sordelet, J. A. Andereg, P. Brunet, J.-M. Dubois, and P. A. Thiel, *Mat. Res. Soc. Symp. Proc.* **553**, 263 (1999).
- ⁸ P. J. Pinhero, J. W. Andereg, D. J. Sordelet, M. F. Besser, and P. A. Thiel, *Phil. Mag. B* **79**, 91 (1999).
- ⁹ P. J. Pinhero, J. W. Andereg, D. J. Sordelet, T. A. Lograsso, D. W. Delaney, and P. A. Thiel, *J. Mater. Res.* **14**, 3185 (1999).
- ¹⁰ V. Demange, J. W. Andereg, J. Ghanbaja, F. Machizaud, D. J. Sordelet, M. Besser, P. A. Thiel, and J. M. Dubois, *Appl. Surf. Sci.* **173**, 327 (2001).
- ¹¹ V. Demange, F. Machizaud, J. M. Dubois, J. W. Andereg, P. A. Thiel, and D. J. Sordelet, *J. Alloys Compd.* **342**, 24 (2002).
- ¹² C. J. Jenks, *Mat. Res. Soc. Symp. Proc.* **553**, 219 (1999).
- ¹³ J. Ledieu, V. R. Dhanak, R. D. Diehl, T. A. Lograsso, D. W. Delaney, and R. McGrath, *Surf. Sci.* **512**, 77 (2002).
- ¹⁴ J. Ledieu, C. A. Muryn, G. Thornton, R. D. Diehl, T. A. Lograsso, D. W. Delaney, and R. McGrath, *Surf. Sci.* **472**, 89 (2001).
- ¹⁵ J. Ledieu and R. McGrath, *J. Phys: Cond. Matt.* **15**, S3113 (2003).
- ¹⁶ R. McGrath, J. Ledieu, E. J. Cox, S. Haq, R. D. Diehl, C. J. Jenks, I. Fisher, A. R. Ross, and T. A. Lograsso, *J. Alloys Compd.* **342**, 432 (2002).
- ¹⁷ J. Ledieu, R. McGrath, R. D. Diehl, T. A. Lograsso, D. W. Delaney, Z. Papadopolos, and G. Kasner, *Surf. Sci.* **492**, L729 (2001).
- ¹⁸ Z. Papadopolos, G. Kasner, R. D. Diehl, J. Ledieu, E. J. Cox, N. V. Richardson, Q. Chen, T. A. Lograsso, A. R. Ross, and R. McGrath, *Phys. Rev. B* **66**, 184207 (2002).
- ¹⁹ S. Haq and D. A. King, *J. Phys. Chem.* **100**, 16957 (1996).
- ²⁰ R. Duschek, F. Mittendorfer, R. I. R. Blyth, F. P. Netzer, J. Hafner, and M. G. Ramsey, *Chem. Phys. Lett.* **318**, 43 (2000).
- ²¹ J. Yoshinobu, H. Tanaka, T. Kawai, and M. Kawai, *Phys. Rev. B* **53**, 7492 (1996).