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A high resolution electron energy loss spectroscopy study of the adsorption of benzylic amide macrocycle on Au(1 1 1)

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Abstract

The adsorption from the gas phase of a macrocyclic molecule composed of benzylic amide (–CONH–CH₂–C₆H₄–) groups on Au(1 1 1) at 300 K has been studied using high resolution electron energy loss spectroscopy. The film order and vibrational properties were explored as a function of coverage, method of adlayer deposition and annealing. Beyond a critical coverage, a template effect strongly influences the macrocycle's orientation with respect to the substrate. In the case of ordered films (domain size > 80 Å), the intensity of the out-of-plane C–H deformation mode relative to the in-plane C–H stretch indicates that an adsorption geometry with the plane of the phenyl rings largely parallel to the Au(1 1 1) surface is favoured in the submonolayer to monolayer coverage regime. Upon consideration of solid state X-ray diffraction data, this flat-lying molecular orientation, which is accompanied by chemisorption via the carbonyl function, must involve considerable distortion of the adsorbed macrocycle from its crystal structure. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electron energy loss spectroscopy (EELS); Gold; Single crystal surfaces; Chemisorption

1. Introduction

There is considerable interest in the preparation and characterisation of functionalised, switchable,

ordered arrays of macromolecules which offer the promise of versatile building blocks for the development of advanced multifunctional materials [1–3]. Recently, Leigh and coworkers have discovered a new class of hydrogen bond assembled interlocking molecular 'rings', catenanes comprising benzylic amide units, in which the mechanical bond holding the components of the molecule together is dynamic and therefore can be used to modify the molecule's properties through external stimuli [4–8]. Controlling the location of a macrocycle between two or more inequivalent sites in catenanes or in their relatives the rotaxanes,

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interlocked structures comprising a central ‘thread’ circumscribed by a macrocyclic ring, represents the first step in the development of components for nanoscale devices such as molecular shuttles, switches and information storage systems [9–12].

Unfortunately, intermolecular hydrogen bonds, the driving force for the formation of these macromolecular structures, result in immobilisation of the component parts in the solid state [13]. However, extraordinary structure-dependent dynamic behaviour, induced by solvent effects and minor structural modifications tuneable in the synthetic strategy, has been observed [3,14]. For example, in the case of benzylic amide [2] catenanes, the molecules readily rearrange in solution by way of an intricate combination of steric effects, cooperative assembly and disassembly of hydrogen bonds, amide bond rotamerization, π -stacking and phenyl–phenyl T-shaped herringbone interactions [14].

Having addressed the question of how to construct ‘molecular machines’, the challenge now is to gain access to and manipulate this unique chemistry to obtain new artificial materials. To this end, the formation and characterisation of two-dimensional ordered arrays of these molecules on solid supports such that they retain their dynamic properties may prove rewarding. Fustin et al. have previously studied the adsorption of benzylic amide [2] catenane on Au(111) [15,16]. The authors report chemisorption of the molecule via the carbonyl moiety of the amide groups at low coverage and a substrate template effect resulting in well-ordered films extending for the very first layers. This adsorption behaviour may be dictated by cooperative intra- and intermolecular hydrogen bonds and π -type interactions between the phenyl rings (as observed in the solid state) with the macromolecules oriented such the carbonyl groups within the first monolayer can make intimate contact with the surface [13]. Hence, the chemisorption may simply be a consequence of the preferred conformation of the two interlocking macrocycles independent of the substrate. Alternatively, the bonding of the carbonyl functions to the Au surface may be primarily responsible for the adsorption geometry adopted. Of course a combination of these two possibilities must also be

considered. Indeed, the occurrence of chemisorption and the results from theoretical studies which suggest deformation of the adsorbed catenane resulting in a deviation from the solid state structure favour a scenario involving a substrate template effect [16,17].

Given that a more detailed understanding of the adsorption processes is limited by the structural complexity of [2] catenane, a study of the simpler component, the prototypical benzylic amide macrocycle (Fig. 1), may provide further insight into the design and assembly of more complex functional layers. In this paper we report on the characterisation of the macrocycle adsorbed from the gas phase on Au(111) at 300 K using high resolution electron energy loss spectroscopy (HREELS). The surface intermediate formed, its molecular orientation as a function of coverage, the film order and growth mechanism are discussed.

2. Experimental

Details of the synthesis of the benzylic amide macrocycle (1,7,14,20-tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane) and the X-ray crystal structure, which is shown schematically in Fig. 1, are given elsewhere [8,18]. The thin films were prepared by vacuum sublimation of the macrocycle on Au(111) at 300 K using a well-outgassed custom built cell consisting of a Pyrex crucible heated resistively to 530 K (close to the macrocycle melting point of 523 K) with the temperature being measured by a chromel–alumel junction fixed at the tube exit. The exposures were monitored using an uncalibrated Bayard–Alpert ionisation gauge.

The Au single crystal ($10 \times 7 \times 2$ mm³) oriented to within 0.5° of the (111) plane (metal crystals and oxides) was cleaned in situ by cycles of argon ion bombardment (0.5 kV, 15 mA) and annealing to ~ 800 K. The surface crystallography and cleanliness were established using LEED and HREELS. After cleaning, LEED revealed a sharp, low background pattern typical of a reconstructed Au(111)-($\sqrt{3} \times 22$) surface [19].

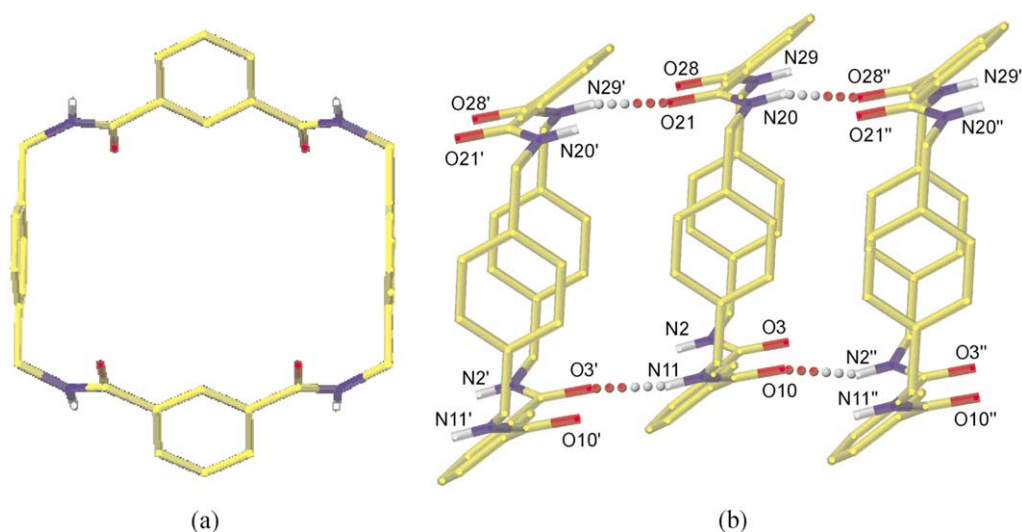


Fig. 1. The X-ray crystal structure [18] of the benzylic amide macrocycle (1,7,14,20-tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexosane) showing the staggered, stacked chair-like conformation adopted in the bulk solid state: (a) a single molecule and (b) a packing diagram. Dotted bonds show intermolecular hydrogen bonds (length: O3'-HN11/O10-HN2''/O21-HN29''/O28'-HN20'' = 2.87 Å; angle: O3'-HN11/O10-HN2''/O21-HN29''/O28'-HN20'' = 150.2°). Colour code: carbon: yellow; nitrogen: blue and oxygen: red.

The HREELS experiments were carried out in an UHV system (SEDRA ISA RIBER) equipped with sample preparation and main analyser chambers operated at base pressures in the low 10^{-9} and 10^{-10} Torr range, respectively. The spectrometer consisted of a 180° hemispherical monochromator and analyser ensemble described in more detail elsewhere [20]. To prevent contamination of the spectrometer vessel, sample annealing and dosing was performed in the preparation chamber. Spectra were recorded at 6.0 eV primary electron beam energy (E_p) in both specular ($\theta_i = \theta_r = 45^\circ$) and off-specular ($\theta_i = 45^\circ$, $\theta_r = 25^\circ$) scattering geometries. The instrumental resolution, defined by the full-width-at-half-maximum (FWHM) of the elastic peak, varied between 12 and 21 meV for this study. All spectra reported here are normalised to the area of the elastic peak in specular geometry.

The solid state Fourier transform infra-red (FTIR) study was performed on macrocycle powder pressed into a pellet in a KBr matrix with a pure KBr pellet as a reference. The data were recorded with a resolution of 2 cm^{-1} using a BIO-RAD FT 60A Fourier transform spectrometer

equipped with a deuterated triglycine sulphate (DTGS) detector.

3. Results and discussion

3.1. Identification of the adsorbed surface species

In the solid state, the benzylic amide macrocycle composed of phenyl rings, amide functions and methylene groups arranges in a staggered, stacked chair-like configuration, as determined by X-ray diffraction. The schematic diagram in Fig. 1 shows that the N–H and C=O bonds are directed towards the next nearest molecule above or below to facilitate intermolecular hydrogen bonding [18]. Understandably the resulting infrared spectrum is rather complex and a detailed assignment of all the peaks is beyond the scope of this paper. Nevertheless, identification of the main vibrational bands (Fig. 2 inset) serves as a reference for the HREELS characterisation of the macrocycle thin films.

HREELS data from a submonolayer coverage (0.1 L exposure) of benzylic amide macrocycle

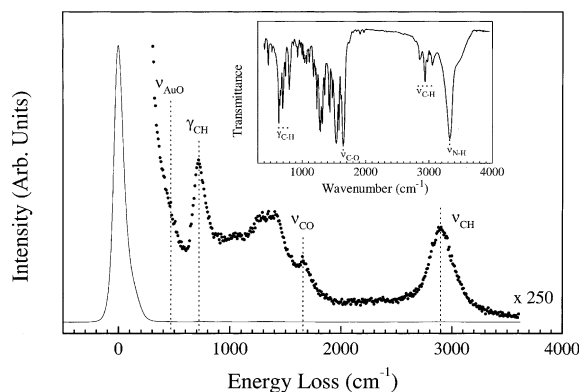


Fig. 2. HREELS spectrum collected in specular scattering geometry ($\theta_i = \theta_r = 45^\circ$) at a primary beam energy of 6.0 eV from benzylic amide macrocycle adsorbed at submonolayer coverage on Au(111) at 300 K. FWHM = 13 meV. Inset: solid state infrared spectrum of the benzylic amide macrocycle.

adsorbed on Au(111) at 300 K is shown in Fig. 2. Upon comparison with the solid state infrared data and a previous HREELS study of benzylic amide [2] catenane adsorbed on Au(111), the main vibrational bands of the parent compound can be identified with the exception of the N–H stretching mode expected at $\sim 3330 \text{ cm}^{-1}$ [15,16,21,22]. The absence of this band is not surprising given the predicted low intensity of this energy loss and its close proximity to the C–H stretching region [15,23,24]. The presence of aliphatic and aromatic groups is indicated by the intense feature at 740 cm^{-1} , which is unambiguously assigned to out-of-plane C–H deformations (γ_{CH}) of the phenyl rings, and the occurrence of C–H in-plane stretching (ν_{CH}) at 2920 cm^{-1} . In addition, a complex group of unresolved low intensity bands extending from 800 to 1600 cm^{-1} originate from C–H in-plane bending, ring breathing and stretching, amide group deformation and C–N stretching vibrations. The C=O stretch (ν_{CO}) is observed at 1685 cm^{-1} . Another feature of particular interest is the weak energy loss superimposed on the tailing elastic peak at $\sim 470 \text{ cm}^{-1}$ attributed to a Au–O stretch (ν_{AuO}) which is more clearly resolved at higher coverages shown in Fig. 3 [25,26].

Fig. 3 shows a sequence of HREELS spectra of benzylic amide macrocycle adsorbed on Au(111)

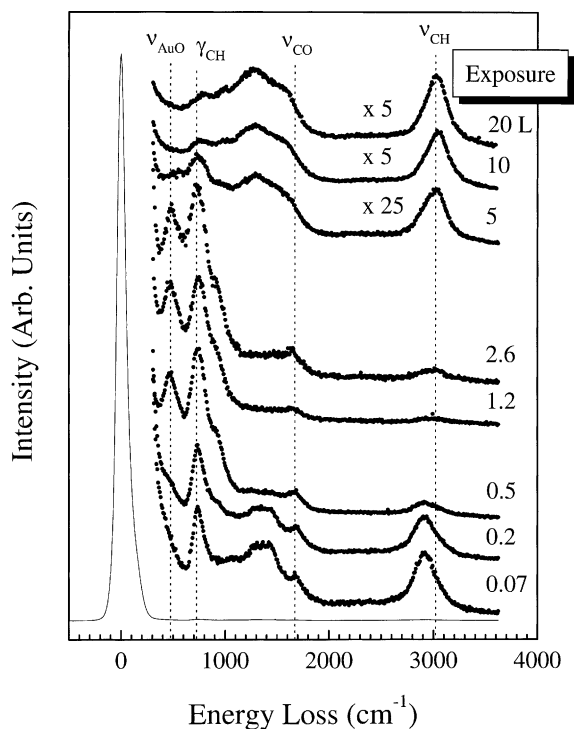


Fig. 3. HREELS spectra collected in specular scattering geometry ($\theta_i = \theta_r = 45^\circ$) at a primary beam energy of 6.0 eV from benzylic amide macrocycle adsorbed at submonolayer to multilayer coverage on Au(111) at 300 K. FWHM = 12–20 meV. The scaling factor is 100 unless otherwise indicated. Exposure to macrocycle vapour are reported in Langmuirs (1L = 1×10^{-6} Torr s).

at 300 K as a function of coverage. Upon increasing the coverage, a dramatic change in the relative intensities of the vibrational bands, which persists throughout the submonolayer regime (0.5–2.6 L exposure), is observed. In particular, the intensity of the phenyl ring out-of-plane C–H bending mode at 740 cm^{-1} increases relative to the C–H in-plane modes at 2920 cm^{-1} accompanied by enhancement of the Au–O stretching vibration. The reverse is true in the case of coverages in excess of monolayer saturation (>2.6 L exposure) which are characterised by the attenuation of the C–H out-of-plane deformation and the Au–O stretching bands in favour of the in-plane modes.

The presence of the ν_{AuO} indicates chemisorption of the macrocycle on the Au surface via the carbonyl function group as reported by Fustin

et al. in the case of [2] catenane films grown on Au(111) [15]. A frustrated z -translation, i.e., vibration of the entire molecule against the surface, would also appear in this region, however, such an energy loss is usually observed with low intensity and hence the band at 470 cm^{-1} is assigned predominantly to Au–O stretching in agreement with previous studies [15,25,26]. The fact that increasing the exposure to form a multilayer film results in the eventual disappearance of this vibrational mode, affirms that it is indeed an interfacial species arising from chemisorption of the macrocycle on the Au surface consistent with X-ray photoelectron spectroscopy characterisation of the films presented elsewhere [27].

Bonding to the surface via the oxygen atoms should give rise to a shift in the carbonyl band to higher or lower frequency depending on the direction of charge transfer between the adsorbate and the substrate. However, in addition to the influence of adsorbate–substrate bonding, intermolecular interactions play a dominant role in the macrocycle film growth mechanism as discussed later in Section 3.4. This leads to ambiguities in interpreting the ν_{CO} band shift of 37 cm^{-1} to higher frequencies (with respect to the solid state IR value) given that amide group intermolecular hydrogen-bonding has been reported to cause such effects, e.g., a red shift of 70 cm^{-1} in the case of the CO stretch for formamide adsorbed on Pt(111) [28]. Hence, any frequency shift due to Au–carbonyl interactions in the case of the macrocycle may be enhanced or attenuated by adsorbate–adsorbate interactions and cannot be interpreted without considerable uncertainty.

It should be noted that an estimate of surface coverage is difficult by HREELS alone, in particular, given the occurrence of adsorbate orientational and ordering changes (discussed in Section 3.2). While exact macrocycle coverages are unknown, the monolayer spectrum was identified by annealing a high coverage sample (Fig. 4a) to 450 K thereby desorbing multilayers leaving only the chemisorbed monolayer on the surface as shown in Fig. 4b. With this reference, spectra corresponding to less than or more than a monolayer in Fig. 3 can be identified with confidence. The characteristic monolayer HREELS spectrum observed following

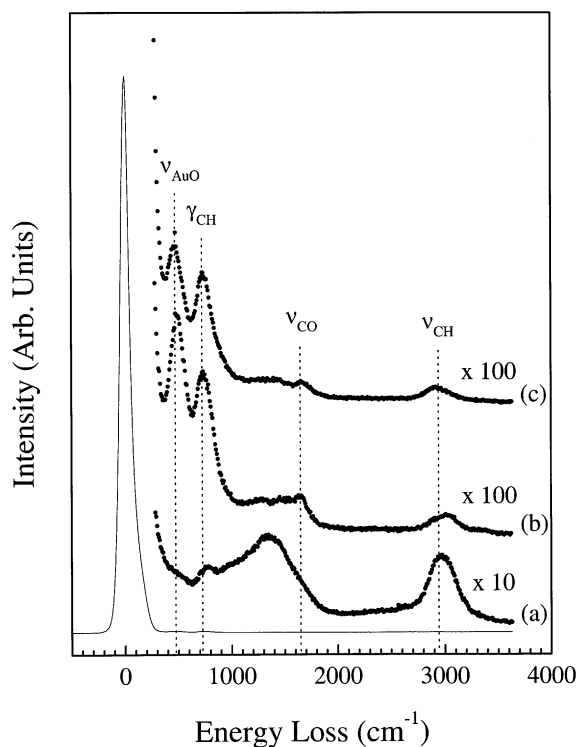


Fig. 4. HREELS spectra collected in specular scattering geometry ($\theta_i = \theta_r = 45^\circ$) at a primary beam energy of 6.0 eV from a benzylic amide macrocycle (a) multilayer film adsorbed at 300 K, (b) monolayer following annealing of a multilayer film to 450 K and (c) monolayer adsorbed at 300 K by controlled sublimation on Au(111). FWHM = 13–20 meV.

annealing of a multilayer sample was reproduced in Fig. 4c by controlled sublimation.

3.2. Determination of the molecular orientation

The metal surface selection rule (MSSR)² can be applied in specular scattering geometry, allowing conclusions to be reached regarding the molecular orientation of the macrocycle with respect to the substrate [29]. In Fig. 5, we compare HREELS spectra collected in specular and 20° off-specular for (a) monolayer and (b) multilayer films. For the monolayer, the γ_{CH} , ν_{AuO} and ν_{CO}

² Only vibrations with a component of the dipole moment change normal to the surface may be observed.

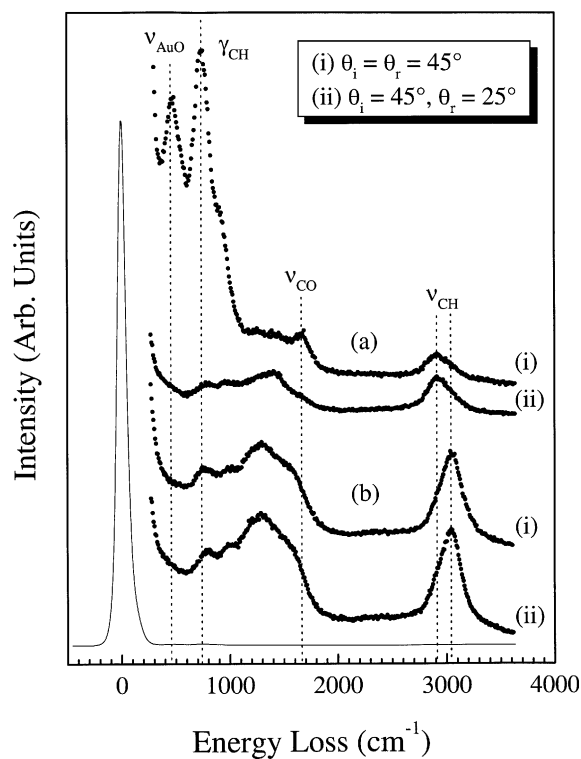


Fig. 5. HREELS spectra collected in specular (i) $\theta_i = \theta_r = 45^\circ$ and (ii) off-specular $\theta_i = 45^\circ$, $\theta_r = 25^\circ$ scattering geometries at a primary beam energy of 6.0 eV from a benzylic amide macrocycle (a) monolayer and (b) multilayer film adsorbed on Au(1 1 1) at 300 K. FWHM = 13–17 meV. The scaling factor is 200 and 10 for (a) and (b), respectively.

bands display a strong normal dipole component as evidenced by a sharp intensity decrease in off-specular scattering geometry (where short range impact scattering occurs) suggesting a preferred molecular orientation of the phenyl rings and amide functionalities.

The attenuation of ν_{CO} and ν_{AuO} bands off-specular indicates that these modes are dipole active and that the carbonyl groups and Au–O bonds are oriented largely perpendicular with respect to the Au(1 1 1) surface. The γ_{CH} band (740 cm^{-1}) has its dipole moment perpendicular to the ring and, hence, in the specular direction this band should be of maximum intensity for a flat-lying macrocycle with the plane of the phenyl rings parallel to the surface. The opposite is true of the in-plane ν_{CH} band (2920 cm^{-1}) which has its dipole moment

change upon vibration in the plane of the ring. Therefore, if we again turn our attention to Fig. 3, we note that with the exception of the two lowest coverages (0.07 and 0.2 L exposures) where both in-plane and out-of-plane C–H vibrations are prominent suggesting a tilted geometry (with phenyl rings inclined with respect to the Au surface) or a mixture of orientations, the γ_{CH} mode is clearly the dominant band from submonolayer to monolayer coverage in agreement with a largely flat-lying macrocycle. In support of this interpretation, the submonolayer and monolayer spectra in Fig. 3 all show a highly asymmetric ν_{CH} feature with a peak maximum at 2920 cm^{-1} implying that the largest contribution originates from the aliphatic components of the molecule as opposed to the aromatic rings which would be expected at higher wavenumbers ($>3000\text{ cm}^{-1}$). Hence, while the increase in the ν_{AuO} loss intensity may be simply due to increasing the surface coverage, the intensity variation between the γ_{CH} and ν_{CH} modes unambiguously signals the occurrence of a coverage dependent reorientation in the submonolayer to monolayer coverage regime from a tilted/mixture of orientations to a largely flat-lying adsorption geometry shown schematically in Fig. 6.

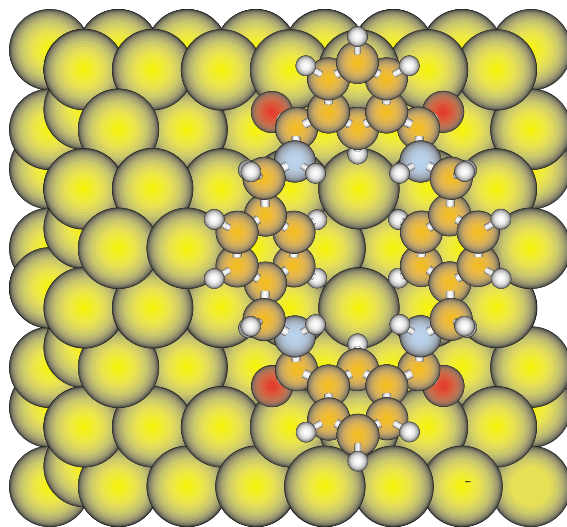


Fig. 6. Schematic diagram of the flat-lying orientation of benzylic amide macrocycle adsorbed at submonolayer to monolayer coverages on Au(1 1 1). Colour code: gold: yellow; carbon: orange; nitrogen: blue; oxygen: red; hydrogen: white.

During the progression from monolayer to multilayer coverage, in-plane vibrational losses become more apparent similar to the initial stage of film growth and the elastic peak intensity decreases (see Section 3.3). Moreover, for the multilayer, the specular and off-specular spectra become almost indistinguishable, as illustrated in Fig. 5b, testifying to the absence of a preferred scattering direction. These results demonstrate that the macrocycle forms disordered multilayers without a preferred molecular orientation most likely due to the lack of intimate contact with the Au surface thus preventing chemisorption.

3.3. Estimation of film order

The crystalline quality of the films can be estimated by measuring the angular dependency of the elastic peak intensity [15,30,31]. The elastic electron scattering from a surface produces Bragg diffraction beams,³ the intensity distribution of which depends on the degree of surface order, i.e., the coherent domain size. Assuming circular domains, the diameter D (Å) can be estimated by [32]:

$$D \cong \lambda / (2\Delta\theta \cos\theta_r)$$

where $\Delta\theta$ (rad) is the FWHM of the angular dependence corrected by instrumental broadening (the intrinsic experimental angular dispersion of the primary electron beam, 1.2° for the spectrometer used in this study), θ_r is the reflection angle and λ (Å) [$= 12.2/\sqrt{E_p}$ (eV)] is the wavelength of the incident electrons. The elastic peak angular dependence has been measured for the macrocycle films as a function of coverage in order to estimate the coherent domain size and gain further insight into the growth mechanism. In Fig. 7 we show the angular profiles of the elastic peak collected for the five lowest exposures (0.07 to 0.26 L) shown in Fig. 3. At the lowest coverages studied, i.e., 0.07 and 0.2 L, where both in-plane and out-of-plane C–H vibrations are prominent, the domain size is 25 and 40 Å, respectively, indicating a decrease in surface order relative to the clean Au(111) substrate. This is followed by an increase in long range

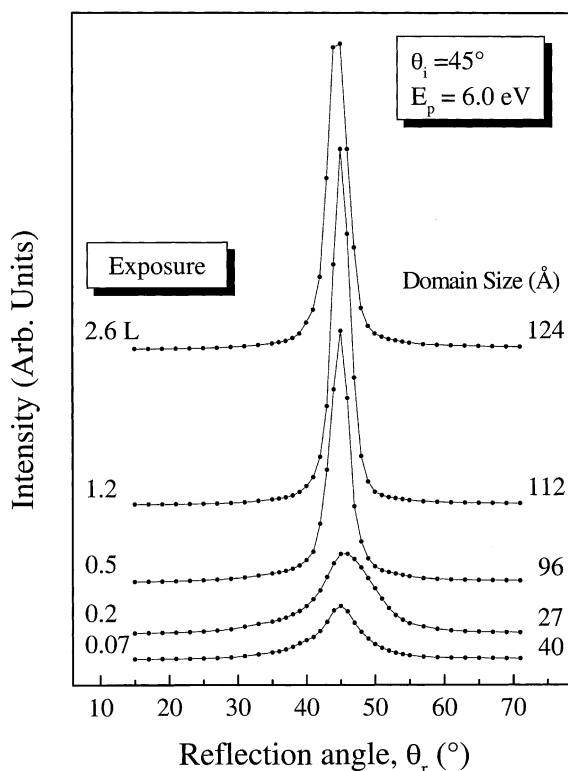


Fig. 7. Angular dependence of the HREELS elastic peak intensity from benzylic amide macrocycle from submonolayer to monolayer coverage adsorbed on Au(111) at 300 K (corresponding to the first five HREELS spectra shown in Fig. 3).

order coincident with the molecular reorientation at higher coverage (0.5 to 2.6 L) with domains of the order of 100–150 Å. These values are comparable with a previous study of a benzylic amide [2] catenane monolayer deposited by sublimation for which the molecule adopts a flat-lying configuration with a domain size of ~ 100 Å [15]. Beyond completion of the first monolayer, the elastic peak angular dependence decreases significantly in intensity and broadens (data not shown) revealing that subsequent macrocycle growth results in a gradual degradation in film order as multilayer formation proceeds.

3.4. Elucidation of the film growth mechanism

In terms of adlayer preparation there are two points of interest. Firstly, the data presented in

³ The elastic peak is the Bragg (0,0) beam.

Figs. 2–5 and 7 involved sublimation on a clean Au(111) surface for each coverage shown. However, sequential deposition can result in entirely different growth behaviour depending on the initial coverage as illustrated in Fig. 8. Fig. 8a shows the sequence of spectra obtained upon sublimation on a pre-existing low coverage (0.1 L exposure, Fig. 2) layer while Fig. 8b depicts those resulting from sequential growth on top of a higher coverage (0.5 L exposure) film. In the first case, where non-parallel molecular orientations prevail in the initial layer, the higher coverages give rise to spectra characterised by suppression of the Au–O stretching vibration, a continuous decrease in the phenyl ring out-of-plane deformation mode intensity and poor film order as evidenced by the absence of any angular dependence in the elastic peak intensity. In contrast, sequential deposition on a film of higher coverage with a larger domain size ($>80 \text{ \AA}$), where the Au–O and phenyl ring out-of-plane deformation modes are dominant, i.e., the macrocycle has assumed a flat-lying, chemisorbed geometry, results in the spectra which are indis-

tinguishable from those obtained by sublimation on a clean surface as can be seen by comparing Figs. 3 and 8b. Hence, it would appear that a critical coverage of macrocycle is required to produce a well-ordered monolayer film of well-defined molecular orientation, i.e., a template effect exists.

It is important to note that annealing a thick multilayer film prepared by either method, i.e., deposition on a clean surface or sequential deposition, to 450 K yields an ordered monolayer of macrocycle as evident from the comparison of Figs. 4b and 8a (solid line). Thus, even by sequential sublimation on a disordered film of small domain size (where the macrocycle coverage was initially less than that required to induce the template effect) a high quality, well-oriented monolayer can be attained by annealing. Furthermore, LEED observations reveal that desorption of multilayers leaving the chemisorbed monolayer leads to formation of an ordered phase with diffuse extra diffraction features [33]. The appearance of additional diffraction features is conclusive evi-

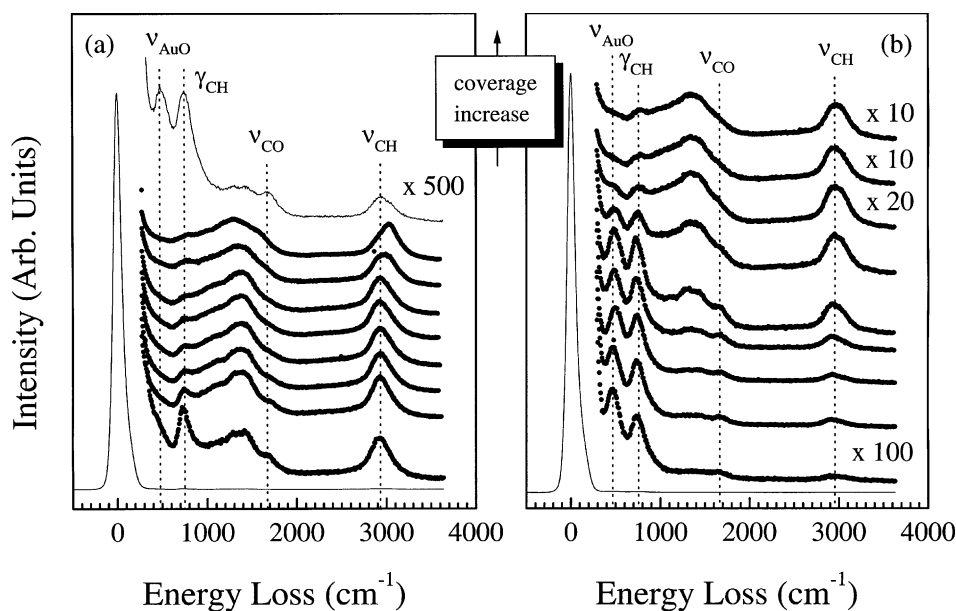


Fig. 8. HREELS spectra collected in specular scattering geometry ($\theta_i = \theta_r = 45^\circ$) at a primary beam energy of 6.0 eV from benzylic amide macrocycle sequentially deposited from submonolayer to multilayer coverage on a (a) disordered (FWHM = 14–21 meV) and (b) ordered (FWHM = 13–14 meV) submonolayer film on Au(111) at 300 K. The full line (—) in (a) corresponds to a multilayer coverage followed by annealing to 450 K. The scaling factor is 100 unless otherwise indicated.

dence of ordering of the monolayer in agreement with our HREELS observations.

Based upon these results we can conclude that a template effect strongly influences the macrocycle film order and molecular orientation. It would appear that a critical coverage is required in order to induce this template effect, with or without annealing. This suggests that adsorbate–adsorbate interactions, which based on the solid state data are predicted to involve primarily intermolecular hydrogen bonding, play an essential role in the film growth mechanism. Moreover, we have observed that in the second and subsequent layers of macrocycle, where only adsorbate–adsorbate interactions occur, a mixture of orientations are permitted. This implies that the Au substrate also contributes to the adoption of a flat-lying geometry in the submonolayer to monolayer coverage regime. Interestingly, annealing of the disordered submonolayer film (0.1 L, Fig. 2) leaves the HREELS spectrum unaltered (not shown) and therefore does not promote ordering. This eliminates the possibility of an activation barrier to the formation of a flat-lying adsorption geometry at 300 K and reaffirms the critical coverage dependence of the ordering phenomena.

The flat-lying orientation of the macrocycle deserves a final comment in relation to its crystal structure. Upon inspection of the schematic diagram shown in Fig. 1, it is clear that the phenyl ring planes are oriented more or less parallel with respect to the C=O bonds of the amide groups such that the dipole moments of the ν_{CH} and ν_{CO} modes are perpendicular to each other. As stated in Section 3.2, attenuation of the ν_{CH} , ν_{AuO} and ν_{CO} modes in off-specular scattering geometry indicates that the C=O and Au–O bonds are oriented perpendicular while the phenyl rings are parallel, with respect to the Au(111) surface, in contradiction with the solid state structure. It follows that, with the majority of phenyl rings arranged largely parallel to the Au(111) surface and anchoring of the carbonyl groups to the surface via the formation of Au–O chemisorption bonds, the adsorbed macrocycle must distort from its preferred solid state structure as shown in Fig. 6 [18].

Interestingly, theoretical studies on the chemisorption of [2] catenane on Au(111) by means of

molecular mechanics calculations using the MM3 method, suggest deformation of the catenane resulting in a deviation from the solid state structure [16,17]. Allowing only the number of chemisorbed oxygen atoms and the geometry of the catenane to vary in the calculation, the most stable conformation was found to consist of one Au–O linkage per macrocycle with some of the phenyl rings almost parallel with respect to the Au(111) surface. Based on HREELS data the authors proposed a substrate template effect [15]. We also find that the macrocycle's adsorption behaviour is not restricted to the preferred conformation of the molecule in the solid state. However, in addition to the influence of adsorbate–substrate bonding, we have discovered that it is in fact adsorbate–adsorbate interactions which play the dominant role in the macrocycle film growth mechanism as demonstrated by the disorder at the lowest coverages studied even in the presence of Au–O bonding. The difference in growth mechanisms can be explained by the fact that for the catenane most of the hydrogen bonding is intramolecular while in the case of the macrocycle the amide groups are available for intermolecular interactions.

4. Conclusions

The results of this HREELS study reveal that the molecular orientation of benzylic amide macrocycle adsorbed on Au(111) at 300 K depends strongly on a critical coverage template effect involving adsorbate–adsorbate interactions, most likely consisting of intermolecular hydrogen bonding. In the case of ordered films, the observation of a prominent out-of-plane phenyl ring C–H deformation relative to very weak in-plane C–H modes allows us to specify a molecular geometry in which the macrocycle is largely parallel with respect to the Au(111) surface plane from submonolayer to monolayer coverages. An adsorbate–substrate contribution by means of Au–O bond formation also influences the film growth mechanism. The molecules in the second and subsequent layers, where chemisorption no longer features, adopt a less selective geometry such that

non-parallel orientations prevail resulting in a decrease in film order.

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