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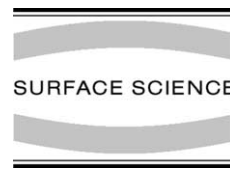
IRAS investigation of a catenane adsorption on Au(1 1 1)

C.A. Fustin [a],[1], S. Haq [b], A. Wingen [a], C. Grégoire [a], R. Raval [b], P. Dumas [c],
J.S. Hannam [d], D.A. Leigh [d],[*], P. Rudolf [a],[*]

[a] *Laboratoire Interdisciplinaire de Spectroscopie Electronique, Facultés Universitaires Notre Dame de la Paix, 61 Rue de Bruxelles, B-5000 Namur, Belgium*
[b] *Surface Science Research Centre, The University of Liverpool, P.O. Box 147, Liverpool L69 3BX, UK*
[c] *Synchrotron Soleil, L'Orme des Merisiers, Saint-Aubin, B.P. 48, F-91192 Gif-sur-Yvette Cedex, France*
[d] *School of Chemistry, University of Edinburgh, The King's Buildings, West Mains Road, Edinburgh EH9 3JJ, UK*

Abstract

The adsorption of a benzylic amide [2]catenane on a Au(1 1 1) single crystal has been studied using infrared reflection absorption spectroscopy. The evolution of the infrared spectra during catenane deposition at different temperatures of the gold substrate (300 and 90 K) has been compared. Evidence of the catenane deformation upon chemisorption have been found at 300 K only. At 90 K the catenane is weakly adsorbed without any deformation.
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Keywords: Infrared reflection absorption spectroscopy (IRAS); Catenane; Chemisorption

1. Introduction

Interlocked molecular rings, or catenanes, first made available through the pioneering work of Stoddart and coworkers [1,2], have been the focus of concerted efforts carried out by many important laboratories world wide [1–8]. The interest in the synthesis and property characterization of supramolecular and molecular interlocked chemical objects derives, on one hand, from the elegant strategies developed for their preparation, and on the other from the possible use of such molecular architectures for molecular machinery or nanotechnology [9–19]. Several of the interlocked structures prepared so far can indeed change the relative positions of their component parts under

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* Corresponding authors. Present address: Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands. Tel.: +31 50 363 4736; fax: +31 50 363 4879 (P. Rudolf).
  E-mail address: p.rudolf@phys.rug.nl (P. Rudolf).
[1] Present address: Unité CMAT, Université catholique de Louvain, Place L. Pasteur 1, B-1348 Louvain-la-Neuve, Belgium.

external stimulus: their macrocycles can circumrotate around one another like the rings of a macroscopic chain and this adds a degree of freedom not available to other systems [9–19]. Different studies have been performed to characterize various types of catenanes but they were carried out almost exclusively in solution and only a very small fraction of effort has been concerned with the solid state properties [18–22]. The formation of ordered arrays of catenanes on solid support is of prime importance if such objects are to be used as molecular machines in the future. To gain further insight on the solid state properties of catenanes we had studied thin films of benzylic amide catenane on Au(1 1 1), characterizing their electronic and vibrational structures by XPS (X-ray photoelectron spectroscopy) and HREELS (high resolution electron energy loss spectroscopy) [23–25]. It was found that relatively well ordered films of this catenane could be grown by sublimation under ultrahigh vacuum and that catenanes of the first monolayer were chemisorbed on the Au(1 1 1) via some of their carbonyl groups.

However, an important issue still needs to be clarified after these studies: experimental evidence for catenane deformation in the first monolayer, which is predicted by molecular mechanics calculations [24], is still needed. The good resolution and chemical sensitivity of infrared reflection absorption spectroscopy (IRAS) prompted us to use this technique in an attempt to answer this question.

In this article, we report on an infrared spectroscopic study of thin films of the [2]catenane depicted on Fig. 1 in order to probe the interfacial interactions between this catenane and the Au(1 1 1) substrate.

2. Experimental

The catenane studied in this work is [2](1,7,14, 20-tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane)-(1′,7′,14′,20′-tetraaza-tetraoxo-3′,5′,9′,12′,16′,18′,22′,25′-tetrabenzocyclohexacosane) which was synthesised as described in Ref. [6]. The X-ray crystal structure of the [2]catenane is shown in Fig. 1.
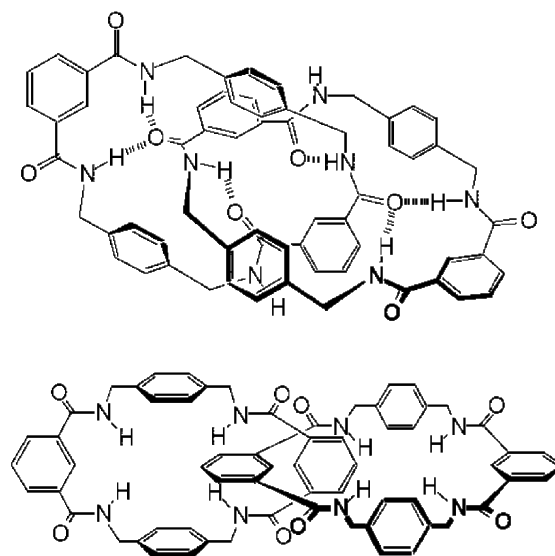

Fig. 1. Schematic drawing showing the X-ray crystal structure of the [2]catenane. Below, the idealized structure illustrating the interlocking of the macrocycles is presented.

The Au(1 1 1) substrate, was cleaned by cycles of Ar$^+$-ion sputtering and annealing until no more contaminants could be detected by Auger and a sharp LEED pattern with the characteristic $23 \times \sqrt{3}$ "herring bone" reconstruction was observed. The catenane was sublimed at about 493 K from a cell composed of a quartz tube of 2 mm of inner diameter and a tantalum filament tightly wrapped around this tube. The cell was initially outgassed at about 423 K for 90 min, and then at 493 K for 15 min.

IRAS experiments were performed in an ultrahigh-vacuum chamber coupled to a Mattson-Galaxy FT-IR spectrometer equipped with a Michelson interferometer and a liquid nitrogen cooled HgCdTe detector. The infrared beam exiting the spectrometer is focused onto the sample using a KBr lens and the reflected beam is first collimated and then focused onto the detector by another set of these lenses. The spectrometer and the detector compartment were continuously purged with dry, CO$_2$ free, air. The resolution of the spectrometer was set to 4 cm^{-1} and typically 400 scans were co-added which gives rise to a total acquisition time of about 2 min per spectrum. The spectrum of the clean substrate was taken as a

background reference R_0 at the beginning of each experiment. Subsequent spectra were recorded in a time evolved mode during catenane deposition and are displayed in transmittance as the ratio of the difference to the background spectrum $(R - R_0)/R_0$. The base pressure in the chamber was in the low 10^{-10} Torr range. Different films were grown while holding the substrate at either 300 or 90 K. Unfortunately, we were unable to extract information from the N—H stretching region because ice formation on the detector element obscured this spectral region.

3. Results and discussion

3.1. Growth at 300 K

Infrared spectra recorded during the growth of a catenane film on a Au(1 1 1) single crystal held at 300 K are shown in Fig. 2. The spectra are displayed in the 900–1900 cm^{-1} range. Below 900 cm^{-1}, the detector response is quite weak, and, accordingly, the associated noise precludes any accurate measurement in this range. Two bands, located at ~1655 cm^{-1} and ~1676 cm^{-1} appear dominantly in the 1000–1900 cm^{-1} frequency range. As the deposition proceeds, the relative intensity of these two bands changes and they broaden. One band, situated at 1676 cm^{-1}, appears clearly before the others and is associated to a carbonyl stretching mode. As the film coverage increases, other bands become discernible at 1655 and 1513 cm^{-1} corresponding to the stretching mode of carbonyl groups and to the stretching mode of C—C bonds in aromatic rings, respectively [26,27]. In the last spectra, a peak appears in the amide II band region (around 1540 cm^{-1}) but its precise frequency cannot be determined because of the noise. There are thus two bands corresponding to a C=O stretching mode: a first one near 1676 cm^{-1}, which is already visible at very low coverage, and a second one near 1655 cm^{-1} which appears when coverage increases and then becomes the dominant feature. This behavior suggests that these two carbonyl bands are linked, one to carbonyl groups of the first monolayer (1676 cm^{-1}), and the other to carbonyl groups
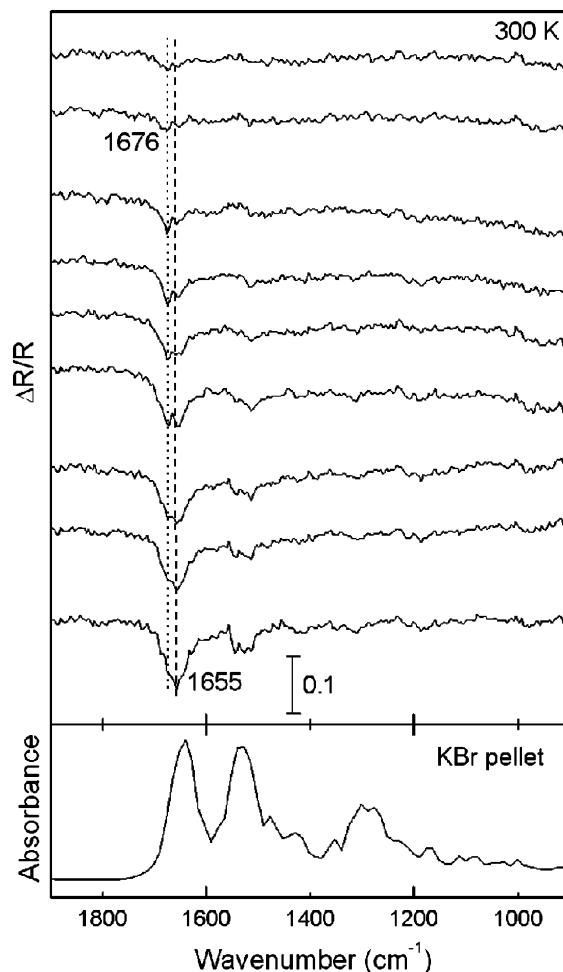

Fig. 2. IRAS spectra recorded during the deposition of catenane on a Au(1 1 1) single crystal held at 300 K. The inset at the bottom shows the catenane infrared spectrum recorded on a KBr pellet.

of the succeeding layers (1655 cm^{-1}). Moreover, a closer look at Fig. 2 reveals that the intensity of the 1676 cm^{-1} peak keeps on increasing when the peak at 1655 cm^{-1} appears. This evolution of the intensities suggests an island growth mechanism where catenanes start to deposit on the first monolayer before the latter is complete. In the solid state (KBr pellet, see bottom inset in Fig. 2) most of the C=O groups are involved in intra or intermolecular hydrogen bonds and there is only one peak at 1642 cm^{-1} for the C=O stretching mode [28].

Catenanes at the interface with the substrate are thus different from catenanes in the bulk. This is in agreement with previous results obtained by HREELS [23] and XPS [24] on such system which showed that catenanes chemisorb on the Au(1 1 1) surface. Fig. 2 does not provide direct evidence of catenane chemisorption but indirect evidence can be extracted. Theoretical calculations using the MM3 method suggested that the catenane structure is markedly modified at the first monolayer level (see Fig. 3) compared to the bulk geometry [24]. This deformation can explain the differences between the C=O of the first layer and the carbonyl moieties of the succeeding layers. More precisely, the differences could be explained by the breaking of the intramolecular hydrogen bonds and by the breaking of conjugation between carbonyl groups and aromatic rings. Indeed, in the first monolayer, there are no hydrogen bonds anymore due to the catenane deformation and this induces a shift of the C=O stretching mode towards high frequencies. Moreover, the deformation changes the angle between the carbonyl plane and the plane of the aromatic ring bearing these C=O groups, which breaks the conjugation between these two groups and raises the frequency of the C=O stretching mode even more [26,27]. Theory and XPS have shown that catenanes of the first monolayer contain only two chemisorbed carbonyl groups [24]. Theory also predicts that those two chemisorbed C=O are pointing downward (Fig. 3). In our IRAS experiments no evidence for these chemisorbed C=O, which were expected at a lower frequency compared to non-chemisorbed carbonyls [29,30], has been found. This could be explained by the small number of chemisorbed C=O groups and/or by a broadening effect. Indeed, the "high" temperature of the sub-
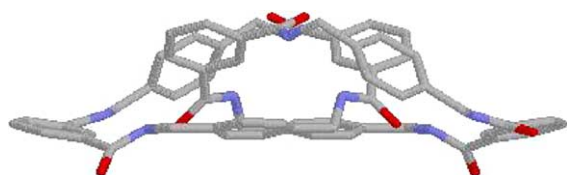
strate and the inhomogeneity of the layer can induce a broadening of the band and hence decrease the peak height [31]. Another possible explanation could be that the chemisorbed C=O do not point downwards as suggested by theory but are more tilted on the gold surface, almost parallel to it, which would then prevent their detection in IRAS.

3.2. Growth at 90 K

Infrared spectra recorded during the growth of a catenane film on the Au(1 1 1) crystal held at 90 K are presented in Fig. 4. In contrast to the growth at 300 K all the bands appear simultaneously and are located at 1637, 1562, 1458,
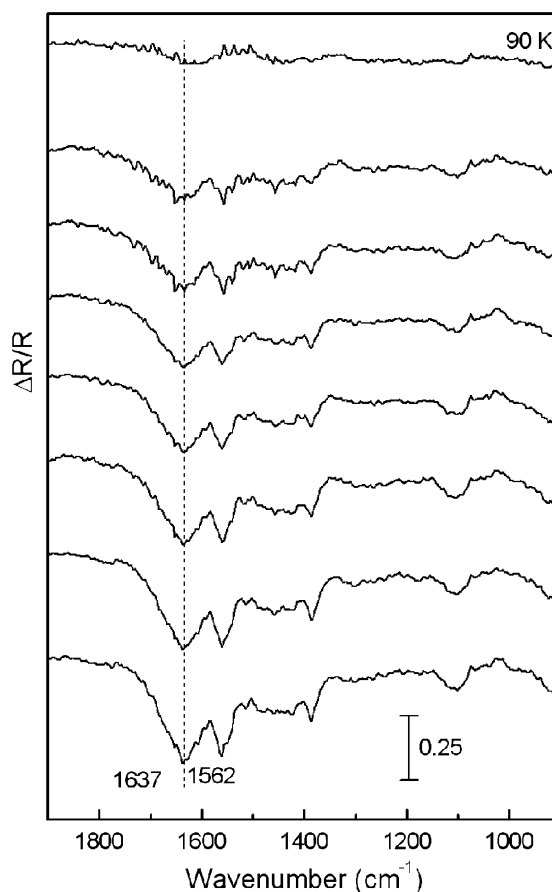
Fig. 3. Structure of a chemisorbed catenane on Au(1 1 1) as determined by MM3 calculations.

Fig. 4. IRAS spectra recorded during the deposition of catenane on a Au(1 1 1) single crystal held at 90 K.

1386 and 1101 cm^{-1}. The first band corresponds to the carbonyl stretching mode, the second one to the amide II band and the other peaks to deformation modes of the aromatic C—H bonds and —CH$_2$— groups. In this case there is only one band corresponding to a carbonyl stretching mode. This suggest that the catenane is not chemisorbed but only physisorbed on the Au(1 1 1) and hence that the first monolayer is not deformed. At this temperature, there is not enough thermal energy for catenanes to deform and they land on the gold surface without changing their geometry. Thus there is no difference between the first monolayer and the succeeding ones and only one band is observed for the carbonyl stretching mode, very close to the solid state value.

At 90 K and at 300 K only one peak is observed for bulk carbonyl groups, but at a different frequency. The frequency of the C=O stretching mode is lower and the amide II band is at higher frequency at 90 K than at 300 K. This shows that, on the average, more or stronger hydrogen bonds are present when the catenane film is grown at 90 K. It is indeed well known that a hydrogen bond weakens the C=O double bond and thus decreases its vibrational frequency. It is also well known that the effect of a hydrogen bond on the amide II band, composed mainly of N—H deformation, is to raise the frequency [26,27]. This difference between 90 and 300 K could be due to a different packing of the catenanes, modifying the strength of the hydrogen bond network. Previous IR studies on salt pellets have indeed shown that the vibrational modes of the catenane amide groups are very sensitive to the environment [32].

4. Conclusion

The growth of benzylic amide catenane films on a Au(1 1 1) single crystal at different adsorption temperatures has been studied by IRAS. At 300 K, the catenanes are chemisorbed on the gold surface. Experimental evidence of the deformation of catenanes belonging to the first monolayer has been obtained. This deformation compared to the bulk geometry breaks the intramolecular

hydrogen bonds and the conjugation between the carbonyl groups and the aromatic ring bearing them. On the other hand, when the Au(1 1 1) is cooled down to 90 K, the catenane is only physisorbed and is not deformed.

Acknowledgments

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