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Experimental and theoretical study of the adsorption of fumaramide [2]rotaxane on Au(111) and Ag(111) surfaces

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Thin films of fumaramide [2]rotaxane, a mechanically interlocked molecule composed of a macrocycle and a thread in a "bead and thread" configuration, were prepared by vapor deposition on both Ag(111) and Au(111) substrates. X-ray photoelectron spectroscopy (XPS) and high-resolution electron-energy-loss spectroscopy were used to characterize monolayer and bulklike multilayer films. XPS determination of the relative amounts of carbon, nitrogen, and oxygen indicates that the molecule adsorbs intact. On both metal surfaces, molecules in the first adsorbed layer show an additional component in the C 1s XPS line attributed to chemisorption via amide groups. Molecular-dynamics simulation indicates that the molecule orients two of its eight phenyl rings, one from the macrocycle and one from the thread, in a parallel bonding geometry with respect to the metal surfaces, leaving three amide groups very close to the substrate. In the case of fumaramide [2]rotaxane adsorption on Au(111), the presence of certain out-of-plane phenyl ring and Au–O vibrational modes points to such bonding and a preferential molecular orientation. The theoretical and experimental results imply that the three-dimensional intermolecular configuration permits chemisorption at low coverage to be driven by interactions between the three amide functions of fumaramide [2]rotaxane and the Ag(111) or Au(111) surface. © 2005 American Institute of Physics. [DOI: 10.1063/1.2137694]

I. INTRODUCTION

Rotaxanes¹ are mechanically interlocked molecules in which one or more macrocycles are locked onto a molecular thread with bulky stoppers at both ends. The "mechanical bond" that holds the components of the molecule together is dynamic, and can therefore be used to modify a molecule's properties through external stimuli, as has been demonstrated using an electric field and light.^{2–4} Hence, rotaxanes are considered as key elements for the development of nanoscale devices with mechanical effects in the macroscopic world. To date, most studies have focused on the behavior of such molecules in solution.^{5–10} It is, however, through controlling their properties in the solid state that rotaxanes offer the

greatest potential as versatile building blocks for the development of advanced materials.¹⁰ Recent studies have shown that rotaxane thin films can be patterned in a controlled way at the nanoscale, an essential feature for information storage applications.¹¹ Rotaxanes have also been proposed as novel photonic molecules, useful for electronic and optical purposes.³

In the present work we investigate the nucleation and growth of fumaramide [2]rotaxane thin films on Ag(111) and Au(111) surfaces. The fumaramide [2]rotaxane comprises a benzylic amide macrocycle mechanically interlocked on a fumaramide thread.⁵ Ag(111) and Au(111) substrates were chosen because for noble metals one expects that molecule-substrate interactions and molecule-molecule interactions are similarly strong so that one does not dominate the other.

This paper focuses on the characterization of fumaramide [2]rotaxane films with monolayer and bulklike coverages, prepared by sublimation in ultrahigh vacuum onto Ag(111) and Au(111) substrates and studied by x-ray photoelectron spectroscopy (XPS) and high-resolution electron-

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FIG. 1. Schematic drawing showing the chemical structure of fumaramide [2]rotaxane.

energy-loss spectroscopy (HREELS). Molecular-mechanics simulations were used to visualize the behavior and three-dimensional configuration of the adsorbed fumaramide [2]rotaxane.

II. EXPERIMENTAL DETAILS

The synthesis of fumaramide [2]rotaxane ([2]-(1,7,14,20-tetraaza-2,6,15,19-tetraoxo -3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane)- (E)-(N,N'-bis(2',2'-diphenyl-ethyl)-2'-butanediamide)rotaxane) has been described elsewhere.⁵ The chemical structure is depicted in Fig. 1.

Ag substrates were prepared by vacuum sublimation onto freshly cleaved mica. The silver layer thickness was 400 nm as determined by a quartz microbalance mounted next to the growing film. The gold substrate was a Au(111) single crystal. Prior to fumaramide [2]rotaxane deposition, the Ag or Au substrate was cleaned in an UHV system (base pressure of 2×10^{-10} Torr) by cycles of argon ion bombardment and annealing until no contaminants could be detected by XPS or HREELS.

Fumaramide [2]rotaxane was sublimed *in situ* onto the substrates kept at 300 K using a custom-built cell which consisted of a Pyrex crucible topped with a 2 mm stainless-steel collimator. The crucible was heated resistively to 470 K with the temperature being measured by a chromel-alumel junction fixed at the tube exit. Exposures were monitored using an uncalibrated Bayard-Alpert ionization gauge. The organic film thickness was such that any interfacial interaction with the substrate is obscured, to the extent that the Ag 3d or Au 4f signal was totally attenuated, and hence we can consider that the photoemission features observed are representative of bulklike solid-state samples. In order to prepare a monolayer film, we first deposited a bulklike film and then annealed it *in situ* to induce desorption of multilayers, leaving a chemisorbed monolayer. This method has been used elsewhere for similar molecules.^{12–14}

The XPS measurements were performed in two different laboratories. The films deposited on silver were analyzed using an X-probe Surface Science Laboratories photoelectron spectrometer with an Al K α monochromatic x-ray source ($h\nu=1486.6$ eV). The energy resolution was set to 1.1 eV and the photoelectron take-off angle was 37°. The films deposited on gold were analyzed using a Scienta ESCA 300 photoelectron spectrometer, also with an Al K α monochro-

matic x-ray source. The energy resolution was set to 0.8 eV and the photoelectron take-off angle was 90°. The binding energies were referenced to the Ag 3d or Au 4f core levels. The base pressure in the spectrometers was in the low 10^{-10} Torr range. Spectral analysis included a Shirley background subtraction for C 1s, linear background subtraction for N 1s and O 1s (see endnote¹⁵), and peak separation using mixed Gaussian-Lorentzian functions in a least-squares curve-fitting program (WINSPEC) developed at Laboratoire Interdisciplinaire de Spectroscopie Electronique, Facultés Universitaires Notre-Dame de la Paix, Belgium. The photoemission peak areas of each element, used to estimate the amount of each species on the surface, were normalized by the sensitivity factors of each element, including analyzer transmission. Three different points of each sample were analyzed to check for homogeneity. Within the error bars quoted, we found the same atomic percentages for all points of the same sample and therefore concluded that all samples can be considered homogeneous.

HREELS data were collected with a Riber Sedra spectrometer equipped with sample preparation and main analyzer chambers operated at base pressures in the low 10^{-9} and 10^{-10} Torr, respectively. The analysis chamber consisted of 180° hemispherical monochromator and analyzer ensemble described in more detail elsewhere.¹⁶ HREELS spectra were recorded with an incident beam energy of 6.0 eV and collected in specular ($\theta_i=\theta_r=45^\circ$) scattering geometry. The spectra presented here were normalized to the specular elastic peak intensity. The instrumental resolution, defined by the full width at half maximum (FWHM) of the elastic peak, was 13 meV for these measurements.

For the molecular-dynamics simulations, we used the same model we employed recently to investigate a variety of other molecular adsorbates on Au(111), where the experimental adsorption energies were reproduced within 1 kcal mol⁻¹. Examples of past applications include (i) the adsorption of alkanes and 1-alkenes on Au(111),¹⁷ where the adsorption energies of short chains, up to C₁₀, were reproduced with an average error of less than 1 kcal mol⁻¹, and the unexpected transition to disorder that occurs for the deposition of alkyl chains between 18 and 26 carbon atoms was explained; (ii) the apparent symmetry breaking of the present macrocycle on the Au surface;¹² (iii) the substitution kinetics of thiols on self-assembled monolayers;¹⁸ (iv) the existence of two surface reconstructions for C₆₀ adsorbed on Au(110),¹⁹ and the adsorption and dynamics of DNA bases on Au(111) where the energies of adsorption were also within 1 kcal mol⁻¹ from the experimental values.²⁰ The model does not require *a priori* definitions of bonds between the atoms of the molecules and those of the metal. The molecules are therefore free to drift on the surface, which can, in turn, reconstruct. The relative simplicity of the approach, which, however, requires the inversion of large matrices, allows the investigation of rather large unit cells. Under the same conditions, the use of modern density-functional-theory-based programs would be too demanding for the present computer hardware, especially for applications where large unit cells are necessary in conjunction with long dynamic runs.

TABLE I. Comparison between the experimental atomic percentages derived from the photoemission peak areas of fumaramide [2]rotaxane and the theoretical values calculated from the stoichiometry of the rotaxane.

Atomic (%)	Theoretical stoichiometry	Multilayer	Monolayer on Au	Monolayer on Ag
Carbon	84.2	84.8±1.7	84.3±1.7	83.1±1.7
Oxygen	7.9	7.5±0.8	7.2±0.8	8.2±0.8
Nitrogen	7.9	7.7±0.8	8.5±0.8	8.7±0.8

The calculations were performed for a single molecule of rotaxane deposited on Au(111) and Ag(111) surfaces. Its structure was minimized using the TINKER molecular-mechanics/dynamics software package.^{21–23} The embedded atom model was used in describing the metal-metal interactions, a MM3 force field for the organic-organic part, and a modified Morse potential [Eq. (1)] in the description of metal-organic interactions.

$$U(r_{ij}) = -\epsilon^* (1 - \{1 - \exp[-A(r_{ij} - r_{ij}^*)]\})^2. \quad (1)$$

In addition, the charge equilibration scheme of Rappe and Goddard²¹ was applied throughout the whole system. This method can be used to study the evolution of partial charges when the chemical environment or molecular geometry changes. The metal-organic interaction model was calibrated to produce experimental desorption geometries and energies of small organic fragments consisting of similar chemical groups that can be found in fumaramide [2]rotaxane. A (111) metal surface model consisting of five layers of 20×20 atoms was used and the lowest layer of metal atoms was kept fixed during the calculations. The top four layers of the surface model were allowed to relax or reconstruct to achieve the lowest energy. Details of the Ag-organic adsorption model will be discussed elsewhere.²⁴

III. RESULTS AND DISCUSSION

A. X-ray photoelectron spectroscopy

Although fumaramide [2]rotaxane is stable at room temperature in air,⁵ it is important to verify that the molecule remains intact when sublimed in vacuum. Photoemission spectra of the C 1s, O 1s, N 1s, Au 4f, and Ag 3d regions were measured for both monolayer and multilayer rotaxane films. In the case of C 1s, O 1s, and N 1s core levels, we observed binding energies and line shapes consistent with the chemical structure and the stoichiometry expected if fumaramide [2]rotaxane adsorbs intact. A quantitative analysis of the fumaramide [2]rotaxane XPS spectra allows us to determine the amount of C, N, and O (excluding hydrogen, which cannot be detected by XPS) on the surface from the photoemission peak areas of each element. The error on the photoemission peak areas was estimated depending on the signal/noise ratio in the spectrum for each element. The carbon signal is better defined; thus the error was found to be 2%. The nitrogen and oxygen signals are weaker, producing noisier spectra, and therefore a more substantial error of 10% was estimated in the peak area. The experimental data presented in Table I show good agreement with theoretically

FIG. 2. X-ray photoemission spectra of the C 1s core levels for: a) fumaramide [2]rotaxane (a) multilayer on Ag(111), (b) monolayer on Ag(111), and (c) monolayer on Au(111). Raw data (■) and fit to the experimental data (—).

calculated values. Hence, we conclude that fumaramide [2]rotaxane remains intact following sublimation in vacuum.

We also checked the stability of the fumaramide [2]rotaxane upon exposure to the x-ray beam and the secondary electrons produced by photoemission in the underlying metal. Upon monitoring the line shape and relative intensity of the C 1s, N 1s, and O 1s core levels as a function of irradiation time, we found no evidence of a charging effect or structural degradation.

Figure 2 shows the C 1s photoemission lines and their mathematical reconstruction for a fumaramide [2]rotaxane multilayer on Ag(111), a monolayer on Ag(111) and a monolayer on Au(111). While rigorously there are sixteen chemically distinct carbon environments in the fumaramide [2]rotaxane, in practice XPS may not distinguish between the various types of phenyl ring carbon. Hence, the mathematical decomposition procedure consists of fitting a minimum number of peaks consistent with the raw data and the molecular structure of the adsorbate with the simplification of assuming equivalent aromatic carbon atoms. In Fig. 2(a), the fit was carried out assuming a molecule with three distinct chemically shifted C 1s core-level emissions occurring at 285.4, 286.3, and 288.8 eV attributed to the aromatic, aliphatic, and carbonyl components. The shake-up structure associated with $\pi-\pi^*$ transitions of the phenyl rings can be observed at 292.3 eV and it represents around 5% of the C 1s signal originated by the phenyl rings, in agreement with the data found for compounds with a similar chemical structure.²⁵ The area ratio for the three distinct components is $\sim 2:3:15$, which is in agreement with the stoichiometry of the molecule. The 1.1 eV binding-energy shift relative to benzene (284.3 eV) (Ref. 26) is understandable given that 17% of the phenyl ring carbon are bound to CH_2NH or NHCO moieties which themselves display C 1s binding energies well within the range reported in literature.^{25,27}

Comparing the multilayer spectrum with the monolayer

FIG. 3. X-ray photoemission spectra of the N 1s core levels for: a) fumaramide [2]rotaxane (a) multilayer on Ag(111), (b) monolayer on Ag(111), and (c) monolayer on Au(111). Raw data (■) and fit to the experimental data (—).

spectra in Figs. 2(a) and 2(b), an additional feature can be distinguished at 286.9 eV. Taking into account the area ratio of the C 1s components ($\sim 1:1:3:15$), the stoichiometry of fumaramide [2]rotaxane and previous studies,¹² we conclude that the carbonyl contribution splits into two peaks at 288.8 and 286.9 eV, suggesting that three amide groups interact with the substrate. Thus, the additional component is reasonably assigned to the carbonyl group involved in Ag–O or Au–O bonding, in agreement with the molecular rearrangement found by the molecular-dynamics simulations (see below). Chemisorption of the oxygen atom to the substrate surface gives rise to charge redistribution in the amide function and, in particular, alters the amount of electronic charge contributed to the C=O bond. The presence of the π - π^* shake-up transition at 292.3 eV indicates that the interfacial bonding does not disrupt the electron conjugation of the phenyl rings; hence, any interactions between the surface and the aromatic groups are weak. There is no difference between the C 1s core level of the monolayer deposited on Au(111) and the one deposited on Ag(111).

In Fig. 3(a) we present the N 1s photoemission line for a multilayer film of fumaramide [2]rotaxane on Ag. The symmetric peak is centered at 400.3 eV and is therefore shifted by 0.5 eV to higher binding energy relative to the reference moiety CH_2CONH (399.8 eV).^{26,27} Presumably, this is a consequence of additional bonding to CH_2 and aromatic groups and perhaps, to a lesser extent, of the involvement in intermolecular hydrogen bonding interactions. Again XPS cannot distinguish between all the different types of nitrogen present in the N 1s spectra; however, their existence is reflected in the FWHM of 1.6 eV, which is larger than the experimental resolution (1.1 eV). Figures 3(b) and 3(c) show the N 1s core-level region for the fumaramide [2]rotaxane monolayer on Ag(111) and on Au(111), respectively. Closer inspection reveals an asymmetry in the N 1s region associated with the amide function. Decomposition of the raw data

FIG. 4. X-ray photoemission spectra of the O 1s core levels for: a) fumaramide [2]rotaxane (a) multilayer on Ag(111), (b) monolayer on Ag(111), and (c) monolayer on Au(111). Raw data (■) and fit to the experimental data (—).

suggests that the N 1s signal of the monolayer films could be fitted by two peaks occurring at 400.3 and 401.4 eV (not shown). However, the peak at 400.3 eV obtained in this way is very broad (~ 1.4 – 1.3 eV). Thus, we tried to fit the N 1s with three components, as shown in the figure, with maxima at 400.2, 400.6, and 401.4 eV. The area ratio of the three components in both monolayers is 3:2:1. This is in agreement with the three-dimensional molecular configuration that arises from the simulations of fumaramide [2]rotaxane adsorbed on the substrate (see discussion below) and allows us to assign the three components with confidence. The peak at 400.2 eV has almost the same binding energy found for the multilayer film and corresponds to unperturbed amide functions. Indeed, fumaramide [2]rotaxane presents three amide groups located far from the substrate, two from the macrocycle and one from the thread. The other two N 1s components correspond to amide groups in close proximity with the substrate, and their difference in chemical shift originates from hydrogen bonds that produce shifts to higher binding energies:²⁸ the spectral feature at 400.6 eV can be attributed to amide groups close to the substrate, one from the macrocycle and one from the thread, which are not involved in hydrogen bonds, and the component at higher binding energy (401.4 eV) corresponds to an amide group from the macrocycle which does form a hydrogen bond.

The O 1s core-level spectra of monolayer and multilayer fumaramide [2]rotaxane coverages on Au(111) and Ag(111) are presented in Fig. 4. The multilayer spectrum [Fig. 4(a)] presents a maximum at 532.0 eV, and its FWHM of 1.6 eV, larger than the experimental resolution, reflects the presence of oxygen atoms in different chemical environments. The symmetrical shape of the peak does not allow the decomposition of the O 1s line shape with confidence. The results for a monolayer on Ag [Fig. 4(a)] and on Au [Fig. 4(b)] are very similar: both monolayer spectra are centered at 531.9 eV and

their FWHM are about 10% larger than that for the multilayer spectrum collected with the same experimental resolution. The latter indicates greater differences in chemical environment for oxygen in the monolayer than in the multilayer. However, from XPS analysis and in contrast with HREELS data discussed below, there is no clear evidence for oxygen interaction with the substrate. Since the entire amide group would feel the loss of charge, it is not possible to discriminate between the situation where only the carbonyl group is bound to Ag or Au and the situation where both oxygen and nitrogen interact with the substrate via their lone pairs.¹³ In fact, in the first case the bonding involves probably the lone pairs of the oxygen and the empty orbital of the metallic surface as seen for the adsorption of acetone on Pt(111).²⁹

B. Molecular-dynamics simulations

The static picture given by the geometry optimization is modified when the effect of temperature is included. Indeed, even short-time molecular-dynamics (MD) simulations (5 ps) for fumaramide [2]rotaxane on both Au(111) and Ag(111) show that the largest changes on partial charges of atoms occur on carbonyl oxygens, on the first-layer metal atoms directly below them and on the hydrogen atoms contributing to the intramolecular hydrogen bonds. On both surfaces, the carbonyl oxygens gain electron density from the surface and become more negative, whereas the closest metal atoms show a loss of electrons. In all cases, the average charge changes on the atoms of the rotaxane are less than $0.1e$, including the hydrogens involved in hydrogen bonds between the thread and the macrocycle. The metal charge changes seem to be of equal magnitude on both surfaces, ranging from $-0.06e$ to $0.115e$ and showing only negligible differences between Ag and Au. The “footprint” of the rotaxane, i.e., how the charge is distributed among the surface atoms, however, is different. On Ag(111), most of the first-layer surface atoms are positively charged, whereas on Au(111) negatively charged metal atoms are also observed. This leads to a smaller electric field on Au(111) than on Ag(111), which was recently found to be in good accordance with surface-enhanced second-harmonic generation (SHG) measurements. The details of this experiment can be found in the work of Arfaoui *et al.*³⁰ In this method the system is bombarded with a Nd:YAG (yttrium aluminum garnet) laser, and frequencies twice the original radiation can be observed due to a lack of symmetry on the surface. Electrical properties such as the field strength and the $\chi^{(2)}(-2\omega; \omega, \omega)$ susceptibility close to the surface can be calculated. The charges of the molecular model system, obtained with the method described in Sec. II, were used to calculate the electric field with the Poisson-Boltzmann algorithms in the DELPHI4 program.^{31,32} This approach yielded an electric field of ~ 15 MV/cm for silver and ~ 7 MV/cm for gold. For silver, this leads to a $\chi^{(2)}(-2\omega; \omega, \omega)$ susceptibility of 23.4 pm/V and is in good agreement with the experimental value of 24.2 pm/V. The resulting field is inhomogeneous, reflecting the charge distribution on the surface atoms. The field is strongest on top of the metal atoms that are directly below

FIG. 5. The average structure of fumaramide [2]rotaxane on (a) Ag(111) and (b) Au(111). The structures were obtained by averaging atom locations of a 5 ps molecular-dynamics run at 298 K. The average structure from the MD runs resembles a collapsed letter X. Color code: carbon=green/black, nitrogen=blue, oxygen=red, and hydrogen=gray.

the carbonyl groups of the rotaxane, and it is unlikely that this feature is strongly dependent on adsorption coverage since it would require a close proximity of carbonyl groups of two adjacent fumaramide [2]rotaxane molecules on the surface. This is hardly the case due to lateral repulsion between the molecules. According to the model, the binding energy of fumaramide [2]rotaxane on Ag(111) is roughly 59 kcal mol^{-1} compared with 86 kcal mol^{-1} on Au(111). The shortest surface normal to the closest nitrogen atom on the fumaramide [2]rotaxane is $2.89 \text{ \AA}$, and the benzene rings are $2.7\text{--}2.8 \text{ \AA}$ above the Ag(111) surface. The corresponding distances on Au(111) are 2.76 and $2.8 \text{ \AA}$. The fumaramide [2]rotaxane orients itself in such a way that there are two or three benzene rings parallel to the surface. The comparison between the optimized structure and the MD simulations reveal that on Ag(111), one of the benzene rings of the macrocycle and one on the thread are parallel to the surface, as shown in Fig. 5(a). This can also be observed on Au(111) where, in addition to the aromatic ring on the thread, there are two benzene rings on the macrocycle that are almost parallel to the surface [Fig. 5(b)]. The macrocycle prefers to lie close to the surface, collapsing the X-like orientation of the molecule that is observed during the geometry optimization. The orientation of the rings is in accordance with the HREELS measurements (discussed below), suggesting that some of the rings are parallel to the surface. These figures also show that there are three amide groups close to the (111) surface, but the charge changes on nitrogen atoms are negligible ($|\Delta q| < 0.01e$). A metal surface reconstruction at 298 K was not observed when averaging the movement of atoms undergoing thermal motion.

FIG. 6. HREELS spectra collected in specular scattering geometry ($\theta_i = \theta_r = 45^\circ$) at a primary beam energy of 6.0 eV from fumaramide [2]rotaxane monolayer (a) and multilayer (b) adsorbed on Au(111) at 300 K. FWHM = 13 meV. Inset: solid-state infrared spectrum of fumaramide [2]rotaxane.

C. High-resolution electron-energy-loss spectroscopy

Since the results obtained by XPS and molecular-mechanics simulations are very similar for both systems, fumaramide [2]rotaxane deposited on Au(111) and on Ag(111), we have chosen to study only one of them by HREELS. Figure 6 shows the HREELS data from monolayer (a) and multilayer (b) fumaramide [2]rotaxane films adsorbed on Au(111). The solid-state infrared data is presented as an inset for comparison. Previous HREELS studies of benzylic amide macrocycle³³ and benzylic amide [2]catenane adsorbed on Au(111)³⁴ and infrared reflection absorption spectroscopy data for benzylic amide [2]catenane adsorbed on Au(111)³⁵ are also taken into account for the assignment of the energy losses.

The expected main vibrational bands can be recognized in the monolayer spectrum. Bands at 730 and 3050 cm⁻¹ signal the presence of aliphatic and aromatic groups. The first band is unambiguously assigned to out-of-plane C–H deformations (γ_{CH}) of the phenyl rings, while the second one corresponds to C–H in-plane stretching (ν_{CH}). Additionally, there is a complex group of unresolved low-intensity bands extending from 800 to 1600 cm⁻¹ that originate from C–H in-plane bending, ring breathing, and stretching vibrations. Of particular interest in the assignment of adsorbate-substrate bonding is the clearly resolved peak superimposed on the tailing elastic peak at 480 cm⁻¹. This band is attributed to a Au–O stretching mode (ν_{AuO}) and can be only explained by the chemisorption of the rotaxane on the Au surface via amide functions, as already inferred from XPS results. A frustrated z transition, 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 480 cm⁻¹ is assigned predominantly to Au–O stretching, in agreement with previous studies.^{36,37} The relative intensities of the γ_{CH} and ν_{AuO} bands (compared with the ν_{CH} band) decrease at higher coverage, consistent with the increased disorder and the absence of Au–O bonding in the multilayer film. The N–H stretching mode (~ 3330 cm⁻¹)^{38,39} is not detected in monolayer

and multilayer spectra. The absence of this band is expected, given that its predicted intensity is very low and occurs close to the ν_{CH} region.^{35,40,41}

Information concerning the molecular orientation of the rotaxane with respect to the substrate surface can be achieved by applying the metal surface selection rule (MSSR) in specular scattering geometry. This selection rule specifies that only those vibrations with a component of the dipole moment change normal to the surface may be detected.⁴² In a detailed HREELS study of fumaramide [2]rotaxane adsorption on Au(111) from submonolayer to multilayer coverages that will be reported in detail elsewhere,⁴³ we could identify the γ_{CH} , ν_{CH} , and ν_{AuO} bands as having strong normal dipole components, evidenced by a significant decrease in intensity in measuring in off-specular scattering geometry. For the monolayer coverage, of relevance to this present report, the γ_{CH} and ν_{AuO} bands disappear in the off-specular measuring mode, implying a preferred molecular orientation of phenyl rings and Au–O bonding via the carbonyl moieties of the amide functionalities. The fact that the out-of-plane γ_{CH} band, which has its dipole moment perpendicular to the phenyl ring and hence should be maximum for phenyl rings parallel to the surface, is observed indicates that at least some of the phenyl rings are oriented parallel to the Au(111) surface in agreement with the molecular-mechanics simulation results. In such an adsorption geometry, it is understandable that the carbonyl moieties can bond to the substrate, thus explaining the observation of the ν_{AuO} band in the monolayer spectrum.

IV. CONCLUSIONS

The present study shows that it is possible to sublime fumaramide [2]rotaxane without decomposition. The C 1s photoemission line of monolayer films reveals that fumaramide [2]rotaxane chemisorbs via three amide functions on Ag(111) and Au(111). XPS results are consistent with the picture proposed by theoretical simulations showing that, on Au(111) and Ag(111) surfaces, fumaramide [2]rotaxane prefers to orient the macrocycle part of the molecule as close to the surface as possible, leading to a “collapsed X-like” structure. According to the molecular-dynamics simulations, fumaramide [2]rotaxane adopts a three-dimensional conformation where two phenyl rings are parallel to the substrate and three amide groups are within bonding distance of it. From HREELS characterization of fumaramide [2]rotaxane adsorption on Au(111), monolayer chemisorption via carbonyl groups of the amide moieties is confirmed by the presence of the Au–O stretching vibration. Furthermore, by comparison of specular and off-specular intensities for out-of-plane C–H deformations, an orientation of the rotaxane with some of the phenyl rings lying parallel to the substrate is revealed.

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