On the Importance of the Headgroup Substrate Bond in Thiol Monolayers: A Study of Biphenyl-Based Thiols on Gold and Silver

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Self-assembled monolayers of a series of ω-(4′-methyl-biphenyl-4-yl)-alkanethiols ($CH_3-C_6H_4-C_6H_4-(CH_2)_m-SH$, $m = 1-6$) formed on polycrystalline gold and silver surfaces were characterized in detail by contact angle measurements, optical ellipsometry, X-ray photoelectron spectroscopy (XPS), reflection absorption infrared spectroscopy (IRRAS), and near-edge X-ray absorption fine structure spectroscopy (NEXAFS). The orientation of the biphenyl moiety, determined by combining the results from IRRAS and NEXAFS, exhibits a pronounced dependence on the number of methylene groups. Similar to *n*-alkanethiols an odd−even effect is observed which on silver is opposite to that on gold. For $m =$ odd on gold and $m =$ even on silver the arrangement of the aromatic moieties agrees well with the bulk structure of biphenyl, and the bonding of the thiols to the substrate is in agreement with an sp^3 hybridization of the sulfur on gold and sp on silver, respectively. In the opposite case of $m =$ even on gold and $m =$ odd on silver, the biphenyl moieties adopt a significantly more canted orientation which, as a consequence, results in a lower coverage. The odd−even behavior of the coverage is in sharp contrast to that seen for *n*-alkanethiols. The experiments provide evidence that a significant driving force exists to pertain the sp^3 and sp hybridization of sulfur on gold and silver, respectively. In the case of gold substrates the experimental results are in conflict with available bending potentials derived from ab initio calculations.

Introduction

Beside the diversity of applications in a variety of fields such as biosensors,[1−3] electrochemistry,[4] or patterning,[5] self-assembled monolayers (SAMs) of thiols adsorbed on metal substrates are also interesting from a fundamental point of view since, even though they are relatively easy to prepare, they represent complex systems with a delicate interplay of mutual interactions between the substrate, the molecules, and the environment. Extensive experimental and theoretical work has been carried out to unravel the principles of film formation and the structure of completed monolayers.[6−20] To date the knowledge of

the building principles of thiol SAMs overwhelmingly relies on investigations of alkane-based thiols from which it was inferred that the structure of thiol SAMs is determined by a balance of intermolecular interactions, e.g., van der Waals (vdW), and the corrugation potential of the interaction of the sulfur with the substrate.[7] As a result, an average spacing of adsorption sites of 5 Å and the optimum vdW distance of ~4.5 Å yields a tilt of the hydrocarbon chains by about 30° away from the surface normal on (111) gold. On (111) silver, even though it basically has the same lattice constant as gold (2.88 vs 2.89 Å), the alkane chains are oriented significantly more upright (0−15°) due to a less corrugated energy hypersurface describing the S−Ag compared to the S−Au interaction. A higher packing density is feasible, and therefore, the vdW interactions reach an optimum for less canted chains. Additionally, such a structure can be affected in different ways by the modification of the tail group. For example, in the case of OH termini a higher

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degree of order results whereas COOH groups increase the gauche conformations.[21]

In a number of studies of *n*-alkanethiols a so-called odd−even effect was found;[22−25] that is, the orientation of the terminal methyl group is significantly different for odd and even numbers of methylene units. Importantly, the effect on gold is opposite to that on silver which suggests that on gold the sulfur exhibits an sp³-hybridization (C−S−Au bending ~104°) whereas on silver an sp-hybridization (~180°) is preferred. In agreement with this observation, surface-enhanced Raman scattering also yields an orientation of the C−S bond largely parallel (perpendicular) to the surface for gold (silver) substrates.[26] Furthermore, the perpendicular orientation of the C−S bond on silver is consistent with sum frequency spectra which lack an asymmetric methyl stretch vibration.[27]

Even though the spectroscopic work suggested that the tilt angle is fundamentally different for both substrates, it is not clear to what extent the metal−sulfur−carbon bond angle (MSC) affects the orientation of the chain. In a theoretical work[13] methanethiol on Au(111) and Ag(111) was investigated. On both substrates the 3-fold hollow sites were found to be energetically most favorable, however, the energy difference between hollow (h) and on top sites (t) being noticeably smaller for Ag than for Au. Whereas for Ag(111) only an sp-type chemisorption mode was reported, two configurations of almost equal energy were found for gold. The sp³-hybridization (MSC ~104°) was calculated to be energetically lower than the sp-hybridization (MSC ~180°) by only 1.72 kJ/mol. The barrier between these minima having a height of 10.47 kJ/mol is at an MSC of ~123°, and it was concluded that an isolated thiolate may easily cross from one bonding geometry to the other.[13] It is important to realize that this theoretical work implies that the MSC for SAMs of alkanethiols is a consequence of the balance between the corrugation of the chemisorption potential and the intermolecular vdW interactions rather than the hybridization of the sulfur excerting a significant directive force and, thus, contributing to the energy balance to a significant extent. In other words, the alkanethiol is considered rodlike with a more or less flexible joint located at the sulfur. Such a behavior is also reflected in models for molecular dynamics and Monte Carlo simulations were the MSC bending potential is considered zero.[14,17,18] Beside the work by Sellers et al.[13] another ab initio calculation of methanethiol on Au(111) was performed which finds the optimum MSC angle to deviate significantly from 104°. Furthermore, no minimum was obtained at 180° in this work.[15,16]

From the experimental and theoretical work, no conclusive picture of the sulfur hybridization has emerged yet. Considering that the bonding of the thiol to the substrate obviously is one of the crucial factors in the structure of thiol SAMs, detailed knowledge of the MSC potential is quite important. This also holds for the modeling of thiol monolayers based on force fields, which relies on results from first-principles calculations of the methanethiol−gold potential energy surfaces.[13] Since a proper ab initio treatment of the gold surface is demanding, as can be inferred from the differences between the work from various groups,[13,15,16,19] an experimental access to thiol−substrate bonding parameters is highly desired. To tackle the issue of the sulfur hybridization, we have synthesized a homologous series of thiols which are characterized by an alkane spacer of varying length between a biphenyl moiety and the thiol headgroup (see Scheme 1 in Supporting Information). In general, thiols bearing an aromatic moiety are interesting from a fundamental point of view. Understanding of how the different cross sections and the increased rigidity of the aromatic unit compared to *n*-alkanethiols affects the film structure may provide deeper insight into the building principles of thiol SAMs. Furthermore, they are appealing from an application point of view since their charge-transfer properties are very different from *n*-alkanethiols, and thus they are interesting systems to modify the surfaces of electrodes.[28−30]

Compared to the vast number of studies on alkanethiols, aromatic thiols have been studied relatively little even though after very scarce studies in the earlier days of thiol SAMs [31,32] the interest has increased significantly throughout the past few years. Besides studies on thiols containing a single benzene unit, oligophenylenes have been studied.[33−38] In particular, Tao et al. have performed systematic studies on thiols with biphenyls or other aromatic systems to reveal their influence on the structure and properties of SAMs.[24,25,39,40] In these studies the aromatic moieties were located very closely to the surface, i.e., either attached directly to the sulfur or separated by one methylene unit.[25] Alkane chains of different length were attached to the opposite site of the aromatic system. For the different compounds, they found nearly identical orientations of the hydrocarbon chains. It was suggested that the herringbone packing of the aromatic moieties determines the lattice and the spacing of the chains[25] and that the sp³ hybridization of the thiolate headgroup is the preferred geometry for thiols on gold.[33] The experiments presented below are complementary to those of Tao and co-workers in a sense that biphenyl-based thiols (CH_3-C_6H_4−C_6H_4−$(CH_2)_m$−SH, $1 \leq m \leq 6$, BPm) are used in which the alkane chains serve as a spacer of varying length between the aromatic moiety and the substrate.

Experimental Section

Substrate Preparation. Polycrystalline gold and silver substrates were prepared by evaporation of 100 nm of gold or

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silver (99.99% purity) onto polished single-crystal silicon (100) wafers with a 5-nm titanium interlayer to improve the adhesion.

Chemicals. *n*-Hexadecane and absolute ethanol were obtained from Fluka and Riedel-de Haen, respectively, and used as received. Biphenyl-substituted alkanethiols with methylene chains varying in length (BP*m*) were synthesized by reacting corresponding bromides with thiourea in ethanol. For $m = 1$, the required 4-bromomethyl-4′-methylbiphenyl was prepared by selective photobromination of 4,4′-dimethylbiphenyl (1.1 equiv of NBS), which was obtained from 4-bromotoluene via a Grignard coupling catalyzed by Ni(PPh$_3$)$_2$Cl$_2$. In the case of $m = 2$, 4-bromomethyl-4′-methylbiphenyl was converted into 2-(4′-methyl-biphenyl-4-yl)ethanol by substitution with NaCN, hydrolysis of the resultant nitrile with H$_2$SO$_4$, and subsequent reduction with LiAlH$_4$. Treatment of the resultant alcohol with CBr$_4$/Ph$_3$P in CH$_2$Cl$_2$ gave the desired 4′-(2-bromoethyl)-4-methyl-biphenyl in good yield. For $m = 3-6$, the corresponding bromides were obtained by cross-coupling of α,ω-dibromides Br(CH$_2$)$_n$Br ($n = 3-6$) with 4-bromo-4′-methylbiphenyl using Li$_2$CuBr$_3$ as catalyst. A large excess of α,ω-dibromides was used in order to achieve predominant formation of the monosubstituted product. The requisite 4-bromo-4′-methylbiphenyl was prepared by a selective cross-coupling of 1,4-dibromobenzene and 4-methyl-phenylmagesium bromide prepared from 4-bromotoluene by using dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium (Pd(dppf)Cl$_2$) as catalyst.

All thiols were characterized by IR, ^{1}H and ^{13}C NMR, and elemental analysis. Experimental details are given in the Supporting Information.

Monolayer Preparation. Freshly prepared substrates were cut into pieces of suitable size (~4−5 cm^2 for IRRAS, ~1 cm^2 for the other techniques), rinsed with absolute ethanol, and immersed into a 1 mM solution of the respective thiol in absolute ethanol at room temperature for 24 h. After removal from the thiol solution, the samples were rinsed with chloroform and pure ethanol and blown dry with argon.

Contact Angle Measurements. Advancing contact angles were measured on freshly prepared samples with a Krüss goniometer, model G1. Millipore water and *n*-hexadecane were used as liquids. The measurements were performed under ambient conditions with the needle tip in contact with the drop. At least three measurements at different locations on each sample were made. The averaged values are reported. Deviations from the average were less than ±1°.

Ellipsometry. The ellipsometer M-44 of J. A. Woollam Co. Inc. was used for the thickness measurements, and the obtained data were analyzed with the respective software. The incident angle was set to 75° and exactly determined with a silicon wafer as a reference. A refractive index of 1.47 was assumed for all films in the calculation of the thickness.[25] The data presented here vary less than 1 Å.

X-ray Photoelectron Spectroscopy (XPS). The XPS experiments were carried out with a Leybold Heraeus LH 12 XPS spectrometer equipped with a non-monochromatic Mg Kα X-ray source (1253.6 eV). The pass energy was set to 23.4 eV, and the spectra were recorded at normal emission with an experimental resolution of about 1.0 eV. The typical operating pressure was less than 4×10^{-9} mbar. All binding energies were referenced to the Au4f$_{7/2}$ position at 84.0 eV. All intensities were determined after subtraction of a linear background and calculated by numerical integration using standard software.

Infrared Spectroscopy. Infrared absorption measurements were performed with a dry-air-purged Bio-Rad FTIR spectrometer, model FTS 175C, equipped with a liquid-nitrogen-cooled MCT detector. All spectra were taken using p-polarized light incident at a fixed angle of 80° with respect to the surface normal. The spectra were measured at a resolution of 2 cm^{-1} and are reported in absorbance units $A = -\log R/R_0$, where R is the reflectivity of the substrate with the monolayer and R_0 is the reflectivity of the reference. Substrates covered with a SAM of perdeuterated hexadecanethiol were used as reference.

Near Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS). NEXAFS experiments were performed at the HE-TGM2 monochromator at the BESSY-1 storage ring in Berlin.[41] The degree of linear polarization of the X-ray light P was 0.92. The NEXAFS spectra were taken at the C1s absorption
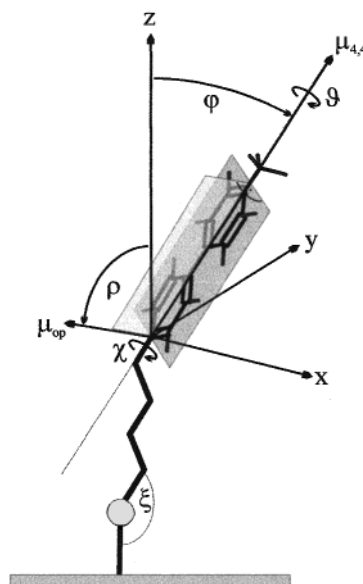

Figure 1. Angles and directions of dipole transition moments used in the characterization of SAMs of ω-(4′-methylbiphenyl-4-yl)alkanethiols. For $\vartheta = 0°$ μ_{op} is in the plane spanned by the *z*- and 4,4′-axes. χ is defined such that, assuming an *all-trans* conformation of the methylene chain, the plane of the hydrocarbon backbone is perpendicular to the plane of the biphenyl if $\chi = 0°$.

edge in the partial-yield detection mode with a retarding voltage of −150 V. The energy resolution was better than 0.8 eV. To determine the molecular orientation, the photon incidence angle of the linearly polarized light was varied between 90° (normal incidence) and 20° or 30°, respectively (grazing incidence). The raw spectra were corrected for the energy dependence of the photon flux by division through the NEXAFS spectrum of a clean gold surface. In the case of the aromatic SAMs on Ag, a spectrum of clean silver was subtracted from the raw spectra before this normalization. From our experience, this procedure gives reliable results for the thiol-derived SAMs on Ag substrate.[42,43] The amount of the substrate signal that was subtracted was normalized to the pre-edge signal for the films adsorbed on silver. For energy calibration the pronounced π*-resonance of graphite (highly oriented pyrolytic graphite, HOPG) at 285.38 eV was used as a reference.

Results

Angles defining the molecular orientation and directions of transition dipole moments (TDM) used to infer the structure of BP*m* SAMs are illustrated in Figure 1. The orientation of the aromatic moiety is determined by the angles ρ and φ which are accessed via NEXAFS and reflection absorption infrared spectroscopy (IRRAS). Both angles are related through the twist angle ϑ according to

$$\rho = \arccos(\sin \varphi \cos \vartheta) \tag{1}$$

The orientation of the *all-trans* alkane spacer relative to the aromatic unit is given by the torsional angle χ and the MSC is defined by ξ. Note, that in the evaluation of the experimental data the orientation of the phenylene rings is characterized by a single value of ρ; i.e., the rings are assumed coplanar, and therefore, an average value for the orientation of the phenylene rings is deduced. From

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Table 1. Vibrational Mode Assignment for BP3 in the Solid State (KBr) and for SAMs on Au and Ag[a]

peak position (cm^{-1})				
KBr	Au	Ag	direction of transition dipole	mode assignment
3023	3029	3028	⊥ 4,4′-axis, ip	C−H str in Ar
2993			⊥ 4,4′-axis, ip	as-CH$_3$ str,
2956 sh	nd	nd	⊥ 4,4′-axis, op	as-CH$_3$ str
2924	2923	2922	∥ 4,4′-axis	as-CH$_2$, s-CH$_3$ (FR)
2856	2866	2867	∥ 4,4′-axis	s-CH$_3$
	2850 sh	2850 sh		s-CH$_2$
2568	nd	nd		S−H str
1498	1501	1500	∥ 4,4′-axis	C−C str in Ar
1397	1381	1380	∥ 4,4′-axis	CH$_3$- sym def
1006	1006	1006	∥ 4,4′-axis	C−H ip bending in Ar
807	nd	nd	⊥ 4,4′-axis	C−H op def in Ar

[a] Only the vibrations relevant for the determination of the molecular orientation are listed. Band assignments are based on refs 45-49. Abbreviations: sh = shoulder, nd = not detected, Ar = aromatic ring, ip = in plane of aromatic ring, op = out of plane of aromatic ring, s = symmetric, as = asymmetric, str = stretching, def = deformation. FR = Fermi resonance
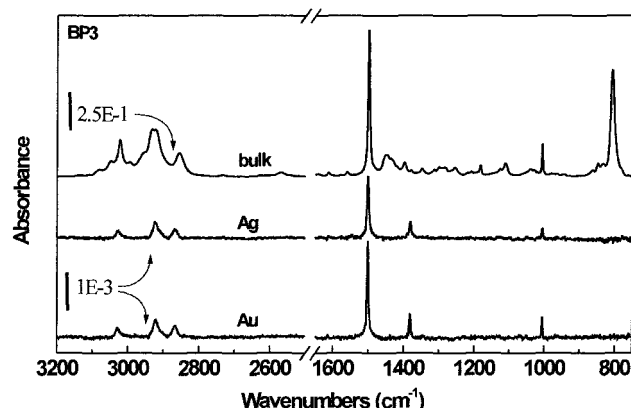

Figure 2. Comparison of IR spectra of bulk BP3 in KBr with SAMs of BP3 on Ag and Au. The bars indicate 2.50×10^{-1} and 1×10^{-3} absorbance units for the bulk and SAMs, respectively.

X-ray diffraction data of bulk biphenyl it is known that there is a torsion of the rings of about ±15° [44] which, however, is smeared out so that an average value of 0° is appropriate.

IR Spectroscopy. Before presenting the spectral behavior of the biphenyl SAMs as a function of the length of the alkane spacer, we illustrate the differences between the bulk-IR and IRRAS spectra on Ag and Au. Assignments are based on refs 45−49.

Figure 2 shows BP3 as a representative example, and Table 1 summarizes the bands relevant for the evaluation of the IRRAS spectra. The bulk spectrum is dominated by two aromatic vibrations at 1498 and 807 cm^{-1} whose TDMs are oriented parallel to the 4,4′-axis and orthogonal to the ring plane of the biphenyl moiety, respectively. Another relatively intense aromatic mode shows up at 1006 cm^{-1} and is assigned to a C−H bending mode with the dipole transition moments μ again along the 4,4′-axis. The weak band at 1397 cm^{-1} is assigned to the symmetric deformation mode of the terminal CH$_3$ moiety.

The range of the C−H stretching consists of two parts: the aromatic and aliphatic bands above and below 3000

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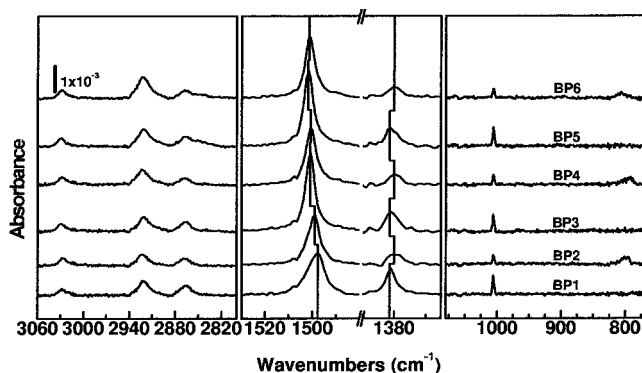
cm^{-1}. The strongest aromatic band at 3022 cm^{-1} is the stretching vibration of the aromatic ring with μ perpendicular to the 4,4′-axis and parallel to the ring plane. The bands below 3000 cm^{-1} comprise both the methylene modes of the alkane spacer and the vibrations of the terminating methyl moiety. The symmetric and asymmetric CH$_2$-stretching vibrations are located at about 2855 and 2924 cm^{-1}. However, these modes are superimposed on the vibrations of the methyl group attached to the aromatic ring. The Fermi resonance of the overtone of the methyl deformation vibration with the symmetric stretch gives rise to bands in the same region.[45−47] In addition a shoulder at 2955 cm^{-1} and a weak band at 2993 cm^{-1} are observed which belong to the asymmetric CH$_3$ vibrations.[49]

Turning to the IRRAS spectra of SAMs of BP*m* on gold and silver, they look very different from the bulk spectrum. Among the bands below 1600 cm^{-1} only three bands are left. Most striking is the disappearance of the intense band at 807 cm^{-1} for both Au and Ag substrates. According to the surface selection rule that only those vibrations are seen which have a component of the TDM perpendicular to the substrate plane, one is tempted to conclude that μ_{IR} (807 cm^{-1}) is oriented mainly parallel to substrate. However, this most simple interpretation has to be taken with a grain of salt for two reasons. First, for transitions oriented toward the substrate plane, the precision is rather limited due to the fact that the intensity scales as cos^2 α (α being the angle between the surface normal and μ) and, thus, changes little around $\alpha = 90°$. Therefore, the uncertainty given by the signal-to-noise ratio easily exceeds 10°. Second, as for all orientations derived from IR spectra, it relies on the assumption that either the absolute value of a TDM or ratios of TDMs from different modes are independent from the state, i.e., bulk sample or SAM. This point is very critical and will be discussed in more detail below together with the NEXAFS measurements. In contrast to the out-of-plane vibration, all other three bands whose transition dipoles are parallel to the 4,4′-axis have significant intensity. Interestingly, the intensity ratio of the bands around 1500 and 1006 cm^{-1} is the same for the bulk and both film spectra within 10−20%, whereas the relative intensity of the methyl mode near 1400 cm^{-1} is higher by a factor of more than 2 in the SAM compared to the bulk.

In the range of the C−H stretching vibrations there are also significant changes. Only the aromatic stretch mode around 3028 cm^{-1} is left. The signatures of the asymmetric CH$_3$ modes are absent and the symmetric CH$_3$ at 2866 cm^{-1} shows up. In the bulk spectrum the symmetric CH$_3$ mode overlaps with the symmetric methylene vibrations

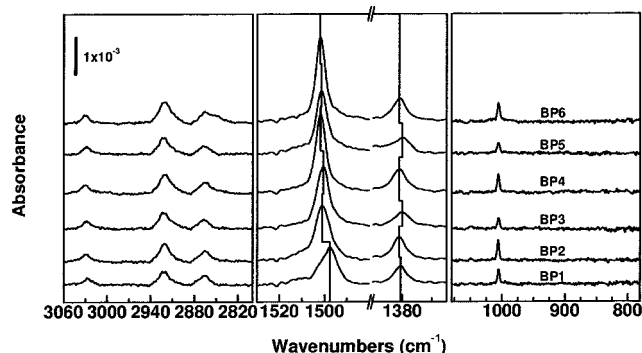**Figure 3.** IRRAS spectra of SAMs of BP*m* on gold with *m* ranging from 1 to 6.

Figure 4. IRRAS spectra of SAMs BP*m* on silver with *m* ranging from 1 to 6.

and only appears as a shallow minimum between the symmetric and asymmetric CH_2 modes.

The IRRAS spectra of the complete series of BP*m* SAMs on gold and silver (Figure 3 and Figure 4) reveal three interesting features. First, the band around 807 cm^{-1}, which in the bulk is very intense, never shows up to a significant extent on Au or on Ag. Nevertheless, a closer look reveals that on Ag no signal at all is detected, irrespective of the length of the alkane spacer, whereas on Au BP SAMs with even numbers of CH_2 groups exhibit a faint signature of the out-of-plane vibration. We will come back to this point further down. Second, looking at the three characteristic bands below 1600 cm^{-1}, there is a pronounced dependence of the band intensities on the number *m* of methylene units. The band intensities alternate with increasing *m* and provide evidence that there is an odd–even effect similar to the intensity variation of the methyl modes of alkanethiol SAMs.[22,23,25,26] Third, on comparison of Ag with Au the odd–even effect is inverted, again analogous to *n*-alkanethiols. Evaluation of the respective band intensities (Figure 5) clearly supports this.

Whereas the odd–even effects of the bands below 1600 cm^{-1} are well developed for all chain lengths, irrespective of the substrate, the band intensities in the range of C–H stretching modes as seen from Figure 6 to some extent depend on the substrate. The symmetric CH_3 at 2866 cm^{-1} is in accordance with bands of the same direction of the TDM at lower wavenumbers. However, the band at 2922 cm^{-1} which is a superposition of the symmetric CH_3 and the asymmetric CH_2 mode behaves differently. Whereas on silver the respective intensity behaves the same way as that of the band at 2866 cm^{-1}, only a general, rather irregular increase due to the increasing number of CH_2 is identified on gold. Therefore, the CH_2 modes somehow compensate the odd–even behavior. No clear alternation of the band at 3028 cm^{-1} is seen either on silver or on gold.
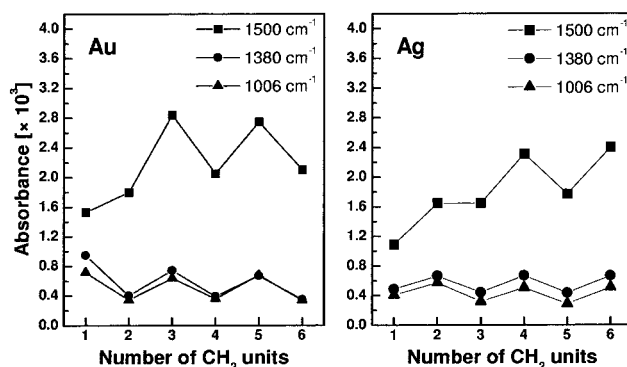

Figure 5. IR band intensities of SAMs of BP*m* on Au and Ag as a function of the number of methylene units of the alkane spacer in the range below 1500 cm^{-1}.
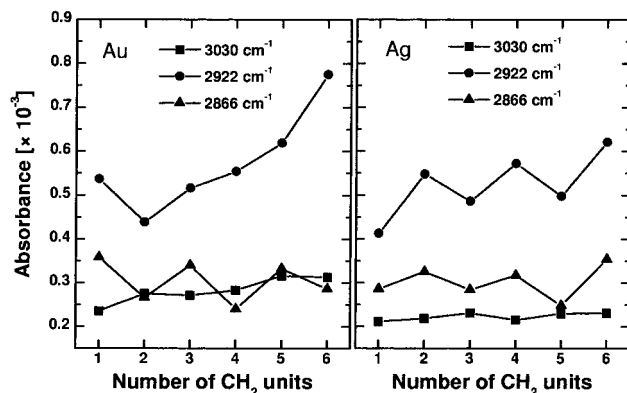

Figure 6. IR band intensities of C–H stretching modes: SAMs of BP*m* on Au and Ag as a function of the number of methylene units of the alkane spacer.

This is surprising since this aromatic band is well separated from any modes of the alkane chain. We have no satisfying explanation for this, but one reason could be that the TDM is affected by the film structure, i.e., changes with the length of the spacer. We note two additional observations. First, the complete lack of the 2956 cm^{-1} feature for all SAM spectra and, second, an odd–even behavior of the asymmetry of the 2866 cm^{-1} band toward lower wavenumbers. The latter indicates that the symmetric CH_2 mode which overlaps with the symmetric CH_3 at 2866 cm^{-1} exhibits an alternation with *m*. As for other bands, a substrate-induced inversion is seen.

For the orientational analysis we rely on the bands below 1600 cm^{-1} since they are well separated from each other and, thus, are easier to evaluate. Furthermore, their quantitative changes are the same even though they originate from different parts of the molecule and represent rather different vibrations. This gives us confidence that changes in intensity of these vibrations really reflect molecular reorientation.

As already mentioned above, the intensity of an IR band of molecules on metal surfaces is given by the projection of the TDM μ onto the substrate normal

$$I_z = |\mu \cos \alpha|^2 \qquad (2)$$

with α as the angle between μ and the substrate normal. An odd–even change in IR intensity of a mode is then given by

$$V = \left(\frac{I_z^{\text{odd}}}{I_z^{\text{even}}}\right)^{1/2} = \frac{\cos \alpha_{\text{odd}}}{\cos \alpha_{\text{even}}} \qquad (3)$$

**Table 2. Orientation of the Biphenyl Moiety in BP*m*
SAMs on Gold and Silver As Deduced from NEXAFS and
IRRAS Data**[a]

		ρ (deg)			φ (deg)	
	V	odd	even	ϑ (deg)	odd	even
Au	1.302(0.11)	79	70	61(10)	23(7)	45(10)
Ag	0.804(0.03)	67	76	54(10)	42(9)	24(6)

[a] The number in parentheses denotes the error. For details see
text.

which, therefore, allows to infer odd−even induced changes
in the orientation of molecular moieties. The average
values for the three bands below 1600 cm^{-1} are listed in
Table 2. Beyond the alternation of their band intensities,
the band positions also reflect an odd−even effect. As
indicated by the solid lines of Figure 3 and Figure 4, the
position of the aromatic band around 1500 cm^{-1} and the
methyl mode at 1380 cm^{-1} vary by 1−1.5 cm^{-1}. Note the
substrate-induced inversion. In contrast, no alternation
is observed for the mode at 1006 cm^{-1}. Even though this
is at the limit of the resolution, it is definitely there and
indicates that lateral interactions play a role.

**Near Edge X-ray Absorption Fine Structure Spec-
troscopy (NEXAFS).** In recent years NEXAFS has
become a very useful technique to determine the orienta-
tion of molecular moieties. As a synchrotron-based spec-
troscopic tool it probes electric dipole transitions from core
levels to unoccupied molecular orbitals close to the
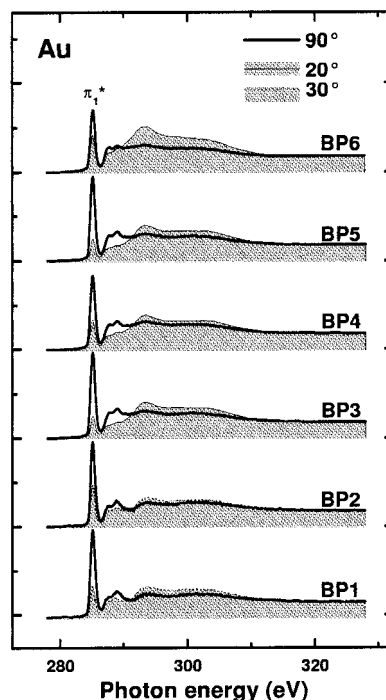continuum.[50]

In contrast to IR spectroscopy, where the components
of the electric field parallel to the substrate surface are
screened on metals, the orientation of dipole transition
moments can be determined directly with NEXAFS by
measuring the dependence of the resonance intensities
as a function of the angle of incidence of the X-ray
radiation.[36] We will come back to this point below when
IRRAS and NEXAFS data are compared.

The C1s spectra for SAMs of BP*m* are shown in Figure
7 and Figure 8 for two different angles of incidence.
Superimposed on the C1s absorption edge which corre-
sponds to transitions into continuum states are several
π^* and σ^* resonances. Referring to the literature for a
detailed assignment of the spectral features,[51] we focus
on the π_1^* resonance at 285.1 eV. This feature which is
related to the aromatic rings in the biphenyl moieties
dominates all spectra. The respective TDM labeled as μ_{op}
in Figure 1 is perpendicular to the plane of the phenyl
rings. A pronounced dichroism of the π_1^* resonance is
observed in all spectra and implies a uniform orientation
of the biphenyl units, i.e., a narrow distribution of tilt
angles. A closer look reveals that analogous to the
vibrational spectra, the alkane spacer produces an odd−
even variation of the angular dependence of the π_1^*
resonance intensity which on gold is opposite to that on
silver.

Assuming a uniform orientation of the molecules, the
intensity of the π_1^* resonance is related to the angle ρ by[52]

$$I(\rho) \propto \left(1 + \frac{1}{2}(3\cos^2\theta - 1)(3\cos^2\rho - 1)\right) \quad (4)$$

θ denotes the angle of incidence of the X-ray radiation.
The quantitative evaluation of the angular dependence of

(50) Stöhr, J. *NEXAFS spectroscopy*; Springer-Verlag: Berlin−
Heidelberg, 1992.
(51) Frey, S.; Stadler, V.; Heister, K.; Zharnikov, M.; Grunze, M.;
Zeysing, B.; Terfort, A. Submitted for publication in *Langmuir*.
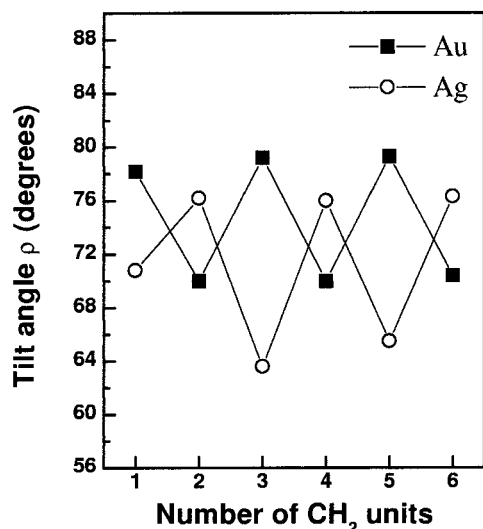(52) Stöhr, J.; Outka, D. A. *Phys. Rev. B* **1987**, *36*, 7891.

Figure 7. C1s NEXAFS spectra from SAMs of BP*m* on gold
at normal (90°) and grazing (20°/30°) X-ray incidence.
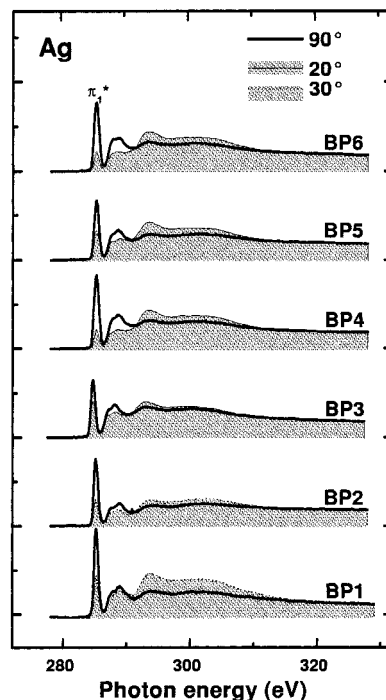
Figure 8. C1s NEXAFS spectra from SAMs of BP*m* on silver
at normal (90°) and grazing (20°/30°) X-ray incidence.

the π_1^* resonance intensity is shown in Figure 9. Note
that in this evaluation we have also taken into account
a small term, $\propto(1 - P)\sin^2\rho$, related to the ellipticity of
the X-ray light. We have not included this term in eq 4
to keep it simple.

It should be mentioned that, like IR spectroscopy,
NEXAFS only yields an average tilt angle of an ensemble
of molecules. If the molecular adlayer contains molecular
subunits with the same electronic structure (e.g., phenyl
units) but different orientations, a direct determination
of ρ for the different species is impossible. In such a case
the angular variation of the NEXAFS intensities has to

Figure 9. Tilt angle of the dipole transition moment μ_{op} of the biphenyl moiety as a function of the length of the alkane spacer for BP*m* SAMs on Au and Ag. Values are derived from the NEXAFS spectra of Figures 5 and 6 based on eq 4.

Figure 10. (a) Plot of ρ vs φ for different values of ϑ. The experimentally determined NEXAFS values of ρ are indicated by the horizontal lines. As illustrated for the case of $\vartheta = 0°$ and the silver substrate, NEXAFS yields an odd−even difference of $\Delta\varphi_N$ whereas the difference $\Delta\varphi_{IR}$ as obtained from the IR data of Figure 5 is significantly larger. The point on the curve for $\vartheta = 32°$ represents the orientation of bulk biphenyl ($\varphi \sim 16°$, $\rho = 76.5°$[72,73]). (b) Plot of $\Delta\varphi_{IR} - \Delta\varphi_N$ calculated from eqs 6 and 7 as a function of ϑ from which the twist angle matching the IR and NEXAFS data is obtained. ϑ is 54° for Ag and 61.5° for Au. The error bars indicate the uncertainty of the experimental values.

be computed for a model structure and the results can then be compared with the experimental data. Besides the case of one molecule per unit cell, a film structure with two molecules per unit cell has to be considered for SAMs of our biphenyl thiols since the bulk of oligophenylenes exhibits a herringbone structure.[53] Furthermore, scanning tunneling microscopy images of a SAM of an aromatic thiol suggest the formation of such a structure.[54] However, as seen from

$$I(\rho) \propto \left(1 + \frac{1}{2}(3\cos^2\theta - 1)(3\cos^2\vartheta \sin^2\varphi - 1) \right) \quad (5)$$

which is derived from eq 4 by using eq 1, NEXAFS, on principle, cannot differentiate between a uniform orientation of the biphenyl moieties and a herringbone structure in which the two molecules per unit cell are characterized by a single value of φ and two twist angles ϑ of equal magnitude but opposite in sign.

Note, that along with an odd−even variation of the angular dependence of the π_1^* resonance intensity there is also a systematic odd−even variation (by $\sim$0.01−0.02 eV) of its energy, which on gold is opposite to that on silver. Although the value of this variation lies within the experimental error, its systematic character proves its authenticity.

Comparison of NEXAFS and IRRAS. The spectroscopic characterization by IRRAS and NEXAFS revealed that the orientation of the biphenyl moiety exhibits a pronounced odd−even dependence on the number of methylene units of the alkane spacer which inverts when changing from Au to Ag.

From comparison of the IRRAS and NEXAFS data the orientation of the biphenyl moiety can be determined since the two techniques are sensitive to TDMs which differ in direction. In NEXAFS the tilt angle φ is given indirectly by ρ since, in general, according to eq 1 ϑ is an additional parameter. Therefore, from the length of the alkane spacer an odd−even induced change $\Delta\varphi_N$ of the tilt angle can be derived, if ϑ is known. From IRRAS an analogous $\Delta\varphi_{IR}$ is obtained. In principle, it can be measured directly, since
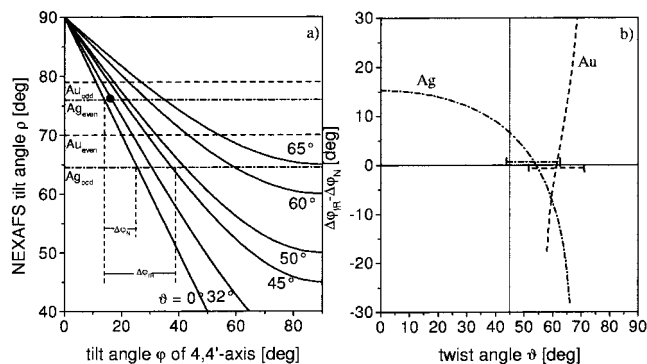
the TDM along the 4,4′-axis is probed. However, this requires knowledge of the absorption cross section. This method, based on absolute values of the TDM, has been applied previously to determine the orientation of molecules in organic monolayers.[55] For reasons discussed below in more detail, we adopt a different evaluation scheme which relies on relative values of band intensities. This method, introduced by Debe,[56] is based on eq 3. Instead of an absolute odd−even difference in φ, we obtain a $\Delta\varphi_{IR}$ which is parametrized by φ. Since $\Delta\varphi_N(\vartheta)$ given by

$$\Delta\varphi_N = \varphi_{odd} - \varphi_{even} = \arcsin\left(\frac{\cos\varphi_{odd}}{\cos\vartheta}\right) - \arcsin\left(\frac{\cos\varphi_{even}}{\cos\vartheta}\right) \quad (6)$$

and $\Delta\varphi_{IR}(\varphi)$ given by

$$\Delta\varphi_{IR} = \arccos(\cos\varphi_{even}V) - \varphi_{even} \quad (7)$$

have to be equal, ϑ and, consequently, φ_{odd} and φ_{even} can be determined. It is important to realize that this evaluation scheme relies on two assumptions. Both ϑ and the IR dipole transition moments are assumed not to vary with the length of the alkane spacer. Whereas for the reasons outlined above we are confident that changes in IR intensities are only due to a reorientation of the molecules, a constant value of ϑ is a rather strong assumption likely not to hold. However, as detailed below this only has a minor effect on the results.

The results of the comparison of NEXAFS and IRRAS data are shown in Figure 10, and the corresponding orientational parameters are compiled in Table 2. A set of curves representing eq 1 is plotted for different values of ϑ (Figure 10a). For comparison and for the discussion presented below, the orientation of biphenyl in the bulk, represented by the solid circle on the curve labeled $\vartheta = 32°$, is included. The horizontal lines represent the average values of ρ from Figure 9. As exemplified for silver and $\vartheta = 0°$, the crossing of these lines with the curves yields the corresponding values of φ from which the odd−even

(53) Kitaigorodskii, I. A. *Organic Chemical Crystallography*; Consultants Bureau: New York, 1961.
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(55) Parikh, A. N.; Allara, D. L. *J. Chem. Phys.* **1992**, *96*, 927.
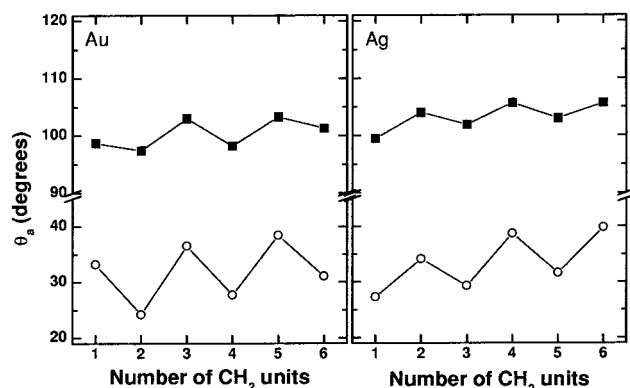(56) Debe, M. K. *J. Appl. Phys.* **1984**, *55*, 3354.

Figure 11. Advancing contact angles of water (■) and hexadecane (○) for SAMs of BPm on Au and Ag.

difference $\Delta\phi_N$ follows. This difference between the tilt angles can now be compared with $\Delta\varphi_{IR}(\varphi)$ from IRRAS. The twist angle ϑ is obtained for $\Delta\varphi_{IR} = \Delta\varphi_N$ and can be inferred from the plot of $\Delta\varphi_{IR} - \Delta\varphi_N$ vs ϑ (Figure 10b). For silver and gold a value of 54° and 61.5° results, and correspondingly, tilt angles φ beyond 40° result for Au/even and Ag/odd. As inferred from Table 2 the odd−even changes of φ are comparable for both substrates (18−22° for the average values). Such a difference in tilt angle between m = odd and m = even has to be paralleled by a significant change of the surface area occupied by a biphenyl unit and, therefore, should affect the packing density. At this point we note that the errors for the angles given in Table 2 arise from the experimental uncertainty of both NEXAFS and IR. Assuming an exact value of ρ the total experimental error appears in the uncertainty of ϑ which is calculated from eqs 6 and 7. The error propagates in the subsequent calculation of φ from eq 1. The nonlinear scaling of the errors due to the trigonometric functions causes the error of φ_{even} on Au above the average value to become undefined which means that an upper limit of φ_{even} cannot be given. Thus the error of 10° means the deviation to smaller values, i.e., the lower limit, is 35°.

As indicated above, assuming that ϑ is not changing with the number of CH$_2$ units is unlikely for the following reason. To match the experimental data for a given value of ρ, φ has to increase if ϑ increases and, therefore, the surface area occupied by a biphenyl unit also increases. Since there is a driving force to maximize the coverage due to the exothermic formation of the S−metal bond, it seems energetically favorable to minimize this surface area, i.e., to adopt a tilt angle as small as possible. If one assumes the extreme case that for m = odd/even on Au/Ag φ is minimized to ∼11°/14°, which is the case for a twist angle of ϑ = 0°, the values of ϑ/φ for the other two cases (m = even/odd for Au/Ag) are still 58°/41° for Au and 51°/39° for Ag. Compared to the model which assumes a ϑ not changing from odd to even numbers of CH$_2$ units, the tilt angles are only slightly reduced.

Regardless of the details of the model, there is a significant change in tilt angle and, thus, in the surface area occupied by a biphenyl unit. As a consequence the packing density should vary significantly with m.

Contact Angle Measurements and Ellipsometry. Both techniques (Figure 11 and Figure 12) also reveal the presence of an odd−even effect. The contact angles of SAMs of BPm thiols are in contrast to n-alkanethiols[22,23,39,57−59] or alkoxy-terminated alkanethiols,[60] where no or only a weak odd−even dependence is observed for hexadecane
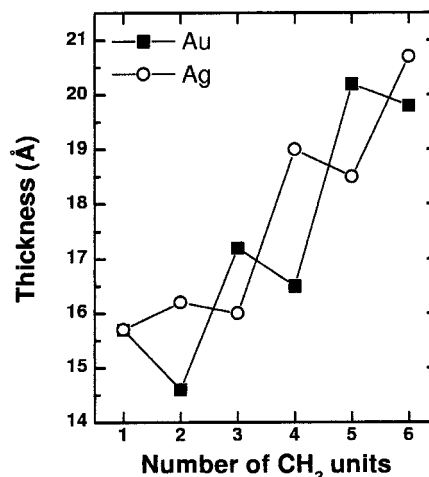

Figure 12. Ellisometric thickness of SAMs of BPm on Au and Ag.

and water. Interestingly, both water and hexadecane contact angles exhibit a distinct odd−even effect which again is different from other systems such as SAMs of alkoxybiphenyl carboxylic acids with long alkane chains (m = 16−19) where hexadecane exhibits an odd−even dependence but water does not.[24] Note that the contact angles for both water and hexadecane change uniformly.

The odd−even variation of the coverage and its substrate-induced inversion expected from the NEXAFS and IR data is confirmed by the ellipsometric data displayed in Figure 12. Assuming that the odd−even effect is solely caused by a change in coverage, an odd−even difference of up to 10% results. This is a fundamental difference to SAMs of n-alkanethiols which exhibit a continuous increase of the signal irrespective of whether the chains contain odd or even numbers of CH$_2$ units.[22,23] On the average, the increase in film thickness per CH$_2$ is in the same range as that for n-alkanethiols. We cannot draw any more detailed conclusions since the accuracy of the data is limited due to the variation in the experimental values and the uncertainty in the indices of refraction. In particular, it cannot be concluded from the data whether the molecules pack more densely on silver than on gold.

X-ray Photoelectron Spectroscopy (XPS). The photoelectron spectra of SAMs of BPm fully confirm the ellipsometric data as can be inferred from Figure 13 which displays the C1s intensities for the series of BPm SAMs. The odd−even effect is superimposed on the overall increase of the thickness of the SAM with an increasing number of CH$_2$ groups. A quantitative evaluation yields a difference of 10−15%. Even though this seems slightly larger than the values obtained from ellipsometry, this has to be considered a good agreement due to the uncertainties of a few percent for both techniques.

As seen from Figure 13, the BP SAMs on Ag also exhibit a variation of the peak position with m. For the more densely packed films the peak is shifted to higher energies by about 0.2 eV. Interestingly, no such effect could be observed for our BPm SAMs on gold. The reason for both the odd−even induced shift on Ag and its absence on Au is not completely clear at present. A packing effect of the band position was also reported for SAMs of n-alkanethiols for which a shift of about 0.1−0.2 eV was detected when

(57) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321.

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(59) Contact angle measurements with hexadecane on alkane thiols on Ag show a weak odd−even effect for chain lengths shorter than ten. See ref 22.

(60) Laibinis, P. E.; Bain, C. D.; Nuzzo, R. G.; Whitesides, G. M. *J. Phys. Chem.* **1995**, *99*, 7663.
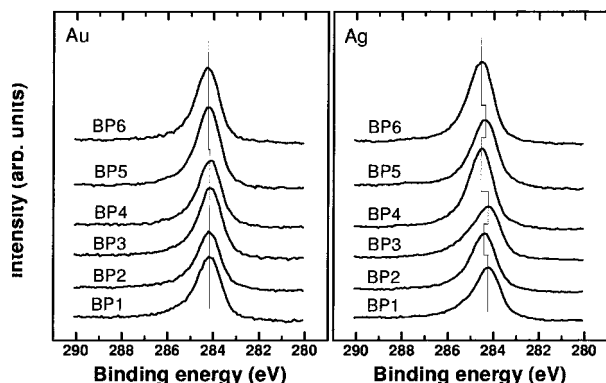
Figure 13. X-ray photoelectron spectra of C1s from SAMs of BP*m* on gold and silver substrates. Whereas on Au no significant variation of the peak position is observed, an odd−even effect is present on silver.

going from pure to amalgamated gold substrates.[61] The amalgamation causes the chains to adopt a more upright orientation and, consequently, a higher packing density. However, the origin of the shift could not be pinned down unequivocally since, as discussed by the authors, different factors can contribute. Another point, which makes the chain length dependent shift even more difficult to interpret, is that the packing density affects resonances close to the continuum rather than the core levels.[62] Nevertheless, if our systems behave analogously to the system investigated by Thome et al.,[61] the density of the layer should be lower on gold compared to silver, in order for the packing effect to vanish. Unfortunatley, as with ellipsometry we cannot decide at present whether the packing density is really lower on gold relative to silver. The problem is that on silver it is much more critical to prepare layers without any residual oxygen and, thus, to exclude any systematic errors in the quantification of an absolute coverage. Experiments focusing on this issue are currently under way.

Since radiation damage can be a serious problem in the evaluation of XPS data of SAMs, we note at this point that the resistivity of the layers to radiation damage is significantly different compared to *n*-alkanethiols.[63] In particular, the S2p signal of biphenyl thiol SAMs exposed to high doses suggests the conservation of pristine thiolate species, in contrast to alkanethiols where X-ray and electron irradiation results in a severe damage of the sulfur−substrate interface.[42,64−66]

Discussion

Since IRRAS is probably the technique used most to infer the molecular orientation, we first comment on its accuracy and possible pitfalls. A crucial assumption in the evaluation of IRRAS data for orientational analysis is that TDMs have to be independent from the state of the molecule. This holds for both the method which relies on absolute intensities of single bands,[55] where a single TDM has to be state-independent, that is, it must be the same in the bulk and in the SAM, and the ratio method introduced by Debe,[56] where ratios of TDMs of different

modes have to be constant. That this has to be validated carefully for each system is evidenced by two observations of our biphenyl thiols. First, as pointed out above, the intensity of the methyl deformation mode below $1400\ cm^{-1}$ relative to the other two modes with their TDMs along the same direction ($\sim$1500 and $1006\ cm^{-1}$) is different for the bulk state and the SAM. The second point refers to the out-of-plane mode of the biphenyl ring at $806\ cm^{-1}$. Being one of the most prominent bands in the bulk spectrum, it basically vanishes in the SAM. In particular, there is no intensity left on silver, irrespective of the length of the alkane spacer (Figure 4). However, on gold some residual intensity is present for even-numbered chains (Figure 3). Usually, such pronounced differences between bulk and SAMs are taken as an argument that the TDM of such a mode is oriented parallel to the metal surface (surface selection rule).[24,37,67,68] Besides the noise-limited accuracy of less than 10° for a TDM close to parallel orientation (see above), an additional limitation requires caution. This is seen by comparing the IRRAS with the NEXAFS data. The TDM of the out-of-plane mode is parallel to the TDM of the NEXAFS resonance and, therefore, allows a direct comparison. Since NEXAFS is not dependent on the comparison of TDMs in different states, it is the method of choice for comparison. For even/odd numbers on Ag/Au with $\rho = 78.9°/76.2°$, one could still argue that noise is the limiting factor. However, for odd/even numbers on Ag/Au where NEXAFS yields $\rho = 66.6°/70.1°$, this is beyond this limit and for silver there still is no intensity at all. Note the additional contradiction that, despite the BP moieties on gold exhibiting smaller tilt angles compared to silver, there is some intensity for even-numbered chains. This can only be explained by a TDM whose magnitude is dependent on its environment. In fact, it is well-known from other systems like CO on metal surfaces that the IR cross section can be significantly altered by a change of the environment, e.g., the inter-molecular distance. Due to dipole coupling and/or local field effects, band intensities can vary appreciably.[69] In our case the difference between Ag and Au is not fully clear but we believe that a somewhat denser packing of the molecules on silver causes the difference. This is corroborated by the XPS data which on Ag shows an odd−even dependence of the energy of the C1s signal whereas on Au no such effect is oberved. As a final remark on this issue we note that there are additional aspects in the quantitative evaluation of IRRAS data. A very recent detailed study on alkane- and terphenylthiols on gold which also exemplifies that TDMs can change and invalidate the evaluation of molecular orientation from IRRAS data comes to similar conclusions and even shows that the preparation procedure of a bulk reference sample is of vital importance.[36]

Turning now to the implications of the spectroscopic results on the structures of the biphenyl SAMs, we start with a comparison between the bulk structure of biphenyls and the film assuming a $\sqrt{3} \times \sqrt{3}$ structure of the sulfur lattice. Even though there is still a debate about how accurately this structure describes thiols on Au(111)[12,16] and a very recent scanning tunneling microscopy work on arenethiols reported an incommensurate structure,[70] it

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(62) Weiss, K.; Bagus, P.; Wöll, C. *J. Chem. Phys.* **1999**, *111*, 6834.
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(67) Han, S. W.; Kim, C. H.; Hong, S. H.; Chung, Y. K.; Kim, K. *Langmuir* **1999**, *15*, 1579.
(68) This argument has also been used in the literature as evidence that the long axis of the aromatic moiety is aligned perpendicular to the surface which, however, is correct only for small twist angles ϑ (see Figure 1) but becomes incorrect for large values.
(69) Chabal, Y. J. *Surf. Sci. Rep.* **1988**, *8*, 211.
(70) Yang, G.; Qian, Y.; Engtrakul, C.; Sita, L. R.; Liu, G.-Y. *J. Phys. Chem. B* **2000**, *104*, 9059.
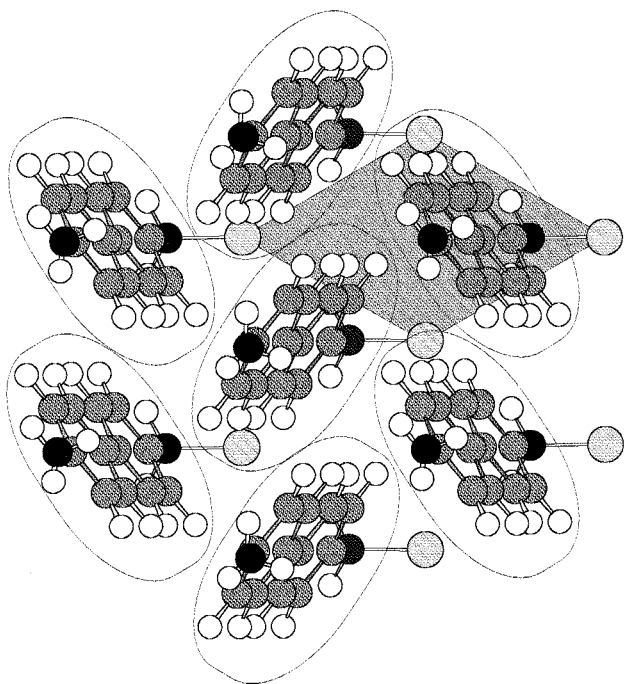
Figure 14. (a) Illustration of the herringbone packing of BP*m* SAMs on gold with odd numbers of CH_2 units. Top view of a BP1 SAM as a representative example. For clarity the methyl groups have been omitted. The ellipses giving an impression of the space filling denote cuts through the aromatic moieties parallel to the substrate and represent the van der Waals dimensions (6.4 × 3.3 Å²). The $\sqrt{3} \times \sqrt{3}$ lattice is indicated by the gray rhomb.

seems to be a reasonable assumption for our thiols since a diffraction study of 4-methyl-4′-mercaptobiphenyl SAMs on Au(111)[71] and high-resolution scanning tunneling microscopy of a phenylethynyl thiol SAM[54] reported a commensurate ($\sqrt{3} \times \sqrt{3}$)R30° structure and, in fact, the $\sqrt{3} \times \sqrt{3}$ lattice of thiols on Au matches the dimensions of the bulk unit cell of biphenyl within about 2%.[53,72,73] In the herringbone pattern, typical for oligophenylenes, the planes of the aromatic rings are rotated by about ±32° with respect to the *y,z* plane and the 4,4′-axis is inclined by about 16° along the *x*-axis.[72,73]

On Au the BP*m* SAM can realize the $\sqrt{3} \times \sqrt{3}$ lattice with values for the biphenyl moiety very close to that for the bulk for *m* = odd. $\varphi = 16°$ and $\vartheta = 32°$ according to eq 1 yields $\rho = 76.5°$, which is very close to the NEXAFS values of 78.9°. An illustration of this structure is provided in Figure 14 with BP1 as a representative example for odd numbers of methylene units. As can be seen, the sulfur atoms match the $\sqrt{3} \times \sqrt{3}$ structure very well. The molecular conformations with respect to the angle χ depicted in Figure 14 have values of $\chi = \pm32°$. These values are not based on any experiment but are chosen since this arrangement is conformationally most likely. Ab initio calculations for the isolated molecule show that the plane of the carbon backbone perpendicular to the aromatic system $\chi = 0°$ is most favorable. The energy for $\chi = 90°$ is higher by about 13 kJ/mol.[74] Since the energy increases approximately as $\cos^2 \chi$, the system will adopt values of χ symmetric around 0°. However, the C−S−Au bond angle ξ is dependent on χ and, therefore, the MSC bending

potential has also to be considered. For $\chi = \pm32°$ values for ξ between 94° and 105° are obtained for *all-trans* methylene chains with *m* = odd. Importantly, changing χ over a range of about 200° causes ξ to vary only by ±10° around 104°, which is the value calculated for the sp³ hybridization of the sulfur on gold.[13]

On silver the NEXAFS value of 76.2° measured for even numbers of CH_2 units perfectly agrees with the bulk value of biphenyl (see Figure 10), and determining the C−S− Ag bond angle analogous to gold gives ∼165°, which is not too far from the value of an sp hybridization angle of 180°.[13] In other words, odd numbers of methylene units on gold and even numbers on silver allow a very favorable arrangement of the molecules with respect to both the bulk structure and the hybridization of the sulfur.

The situation is very different for the other two cases, i.e., odd/even on Ag/Au. Due to the significantly larger tilt and twist angles, the surface area occupied by a BP unit is too large to fit to a $\sqrt{3} \times \sqrt{3}$ for Au or an even denser structure as found for *n*-alkanethiols on Ag.[7] Furthermore, on gold the C−S−metal angle strongly deviates from the sp³ value. A value of more than 130° is found if one assumes an *all-trans* conformation of the alkane spacer. Note that under this condition this value is independent from χ since for *m* = even the C−S bond is essentially parallel to the bond linking the alkane chain and the BP unit. On silver the situation is less clear since, depending on χ, the C−S- substrate angle varies strongly, thus making a prediction difficult. However, the maximum value of ξ being less than 155° suggests that a significant distortion of an sp geometry is associated with *m* = even on silver.

An important conclusion from the pronounced orientational change of the biphenyl units with the number of methylene units, the substrate induced inversion of the odd−even effect, and the chain length dependence of the coverage is that the bending potential of the C−S− substrate bond plays a role significantly more important than previously assumed in the modeling of these layers[14,32,40] or concluded from the modeling of alkanethiols.[18] Our results strongly corroborate earlier experimental work on *n*-alkanethiols which explained the odd−even effect of the orientation of the methyl group and its substrate- induced inversion by sp and sp³ hybridization of the sulfur on silver and gold, respectively.[22,23,25] Our results also confirm the finding by Tao et al.[33] who concluded from R−O−phenyl and R−O−biphenyl thiols (R = H, OCH_3, $OC_{16}H_{33}$) with no or one CH_2 spacer that the sulfur on gold prefers the sp³ hybridization. Using reductive de- sorption, they found that for R = H and OCH_3 the SAMs of thiols without methylene spacer have a significantly lower coverage compared to the thiols with the CH_2 group. Whereas in this case one could argue that these two molecules cannot be compared because the sulfur directly attached to the aromatic system is electronically different compared to being separated by one CH_2 unit, our experiments provide an unambiguous support for their interpretation. However, the argument given that intro- ducing a CH_2 group introduces flexibility and relaxes the rigidity of the thiol headgroup[33,75] is not valid. It is mainly the match of the favorable orientation of the biphenyl moieties with the respective hybridization which is achieved by choosing *m* appropriately. Otherwise, for our BP*m* SAMs one should observe a continuously decreasing odd−even effect with increasing length of the alkane spacer. Nevertheless an increasing number of methylenes is expected to introduce some flexibility and a continuous

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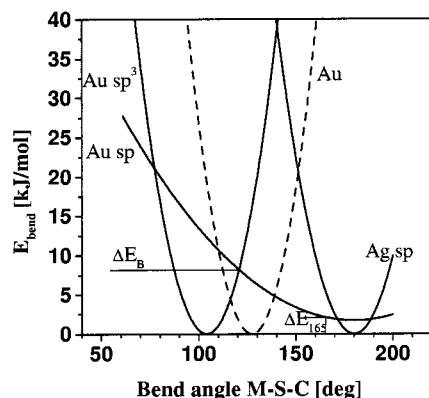(75) Jung, H. H.; Do Won, Y.; Shin, S.; Kim, K. *Langmuir* **1999**, *15*, 1147.

Figure 15. Bending potential of the substrate–S–C angle. Data are taken from ref 13 (solid lines) and ref 16 (dashed line).

change of the conformation with increasing m might account for the masking of the odd–even effect of the band at 2922 cm^{-1} on gold (Figure 6).

Interestingly, the difference in coverage between the biphenyl SAMs with and without CH$_2$ spacer vanishes for R = OC$_{16}$H$_{33}$,[33] which suggests that the interaction energy of the long alkoxy chains is large enough to compensate for the energy required to change the MSC. Similar to our SAMs, a shift to lower wavenumbers for those thiols packing less densely was also observed. Whereas the experiments by Tao et al.[33] are along our results, a study by Chang et al.[25] yields results, unexpected in view of ours. On study of the odd–even effect of 1-(4′-alkoxy-biphenyl-4-yl)methanethiols (CH$_3$(CH$_2$)$_l$–O–C$_6$H$_4$–C$_6$H$_4$–CH$_2$–SH, l = 4, 5, 16, 17), no inversion is seen when changing the substrate from gold to silver, even for the short chains which fall in the length range of spacers of our BPm thiols. A possible reason for this different behavior is the different molecular structure. In our case, the biphenyl is rather symmetrically substituted whereas in the other case the oxygen introduces a dipole moment and, thus, a repulsive contribution is introduced by the alkoxy group. However, whether the different dipole moment can account for the difference between the two systems is not certain at present and has to await a systematic variation of the spacer for 4′-alkoxy-substituted biphenylalkanethiols.

Discussing our results in view of the results from the theoretical work, we stress again that on gold the theory[7,13] treats the C–S–substrate bending as a rather flexible joint. This is seen from Figure 15, which shows the bending potentials according to the data from the ab initio calculations.[13] Since the curvature of the bending potential of the sp-hybridization is rather small, a transition between sp and sp^3 with an activation energy ΔE_B of about 8 kJ/mol at $\xi \sim 120°$ can occur easily. On the basis of these results the coexistence of both types of bonding was proposed. However, the odd–even dependence of our BPm SAMs is incompatible with these potential curves. On gold the bulklike arrangement of the biphenyl units yields a bond angle around 104° for m = odd whereas for m = even a value of ~165° is required. According to Figure 15 the difference ΔE_{165} between these two configurations is less than 3 kJ/mol. Therefore, there is no significant driving force for the SAMs with m = even to adopt a structure with a biphenyl moiety significantly more tilted compared to m = even and, as a consequence, with a lower coverage. Taking an odd–even variation of the coverage of about 10% as deduced from XPS and ellipsometry, and 185 kJ/mol for the Au–S bond,[7] one can estimate the increase in energy of the system for the unfavorable number of methylene units at about 15–20 kJ/mol. Note that this

value is considered a lower limit since an additional contribution comes from the interaction of the aromatic units which is expected to decrease with decreasing coverage. We are left with a discrepancy by a factor of at least 5 in the energy balance between the theory and our experiments. Therefore, the validity of the sp potential curve has to be questioned. The discrepancy could be removed if the minimum of the sp curve were shifted to significantly higher values relative to the corresponding value of the sp^3 curve or if the force constant were changed to about twice the value of the sp^3 geometry. In contrast to gold, our experimental results are compatible with the ab inito calculations for silver[13] (see Figure 15). It is interesting that other ab initio calculations[15,16] of CH$_3$SH on Au(111) yield different results. No stable minimum at 180° was found; the MSC deviates from 104° and is strongly dependent on the site. For the energetically most favorable face-centered cubic site, an angle of 127° was found, whereas the hexagonal close packed site, which is only 3.4 kJ/mol higher in energy, favors 158°. On comparison of these data with the 104° and 165° for our BPm SAMs, an odd–even effect of the orientation of the biphenyl moiety and the coverage is not expected, either.

So far the discussion has only considered the distortion of the bond angle which is relevant for the discussion of the energetics of the system. However, there is an additional degree of freedom for the energetically less favorable BPm SAMs, i.e., m = even on Au and m = odd on Ag, which is the adsorption site. There should be a balance between the displacement of a thiol molecule from its most favorable adsorption site in favor of an optimization of the bond angle. This means that the $\sqrt{3} \times \sqrt{3}$ structure which fits very well to the biphenyl bulk lattice should change to an incommensurate lattice with different adsorption sites. This should be reflected by the electronic structure of the sulfur and indeed, as presented in a forthcoming publication,[76] high-resolution X-ray photoelectron spectroscopy reveals an odd–even effect both in the binding energy and width of the sulfur signal. We close the discussion by noting that the observation of a directive force is not unique to the thiol SAMs presented here but has also been observed recently for thiols consisting of a perfluorinated alkane chain attached to an alkanethiol unit.[43,77] Since upright standing fluorocarbon chains have a larger diameter than the alkane chains, they determine the lattice constant of the layer and separate the hydrocarbon chains beyond the vdW distance. If the C–S–substrate tilt angle is irrelevant, a uniform chain tilt is expected, irrespective of the substrate. In contrast, the experiments yield a substrate-dependent orientation of the hydrocarbon chains equal to the case of simple *n*-alkanethiols.

Conclusion

In addition to the factors already known to enter the energy balance of thiol SAMs, such as intermolecular forces, the surface–thiolate interaction potential, and interactions of the thiolate with the environment, the bending potential of the substrate–sulfur–carbon angle has been identified to contribute significantly. There is a clear preference of an sp^3 and sp hybridization of the sulfur on gold and silver, respectively. On gold, the alternation of the coverage and the orientation of the biphenyl unit with the length of the alkane spacer are in conflict with

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the bending potentials derived from ab initio calculations. Our experiments, which probe the potential of the substrate−sulfur−carbon angle, show that there exists a significant directive force due to the sulfur hybridization. Since a proper modeling of a gold substrate based on first principles is critical as seen from the work published,[13,15,16,19] further effort seems necessary to accurately describe the thiolate−substrate interactions. This also has consequences for molecular dynamics and Monte Carlo simulations of thiol SAMs since they rely on the ab initio data.

For an optimization of the structure of a thiol SAM which requires the control of the molecular orientation and packing density, a suitable molecular structure either has to have intermolecular interactions sufficiently large to overcompensate an unfavorable bonding geometry or has to take the substrate into account. The former can be realized by introducing dipole moments and/or hydrogen bonds, or just by extending the size of the molecule but might have limitations for certain applications such as the control of the interfacial electronic properties. With respect to the structural characterization the experiments also demonstrate that the analysis of SAMs by IRRAS has pitfalls and requires caution.

Supporting Information Available: Synthesis of the ω-(4′-methylbiphenyl-4-yl)alkanethiols ($CH_3-C_6H_4-C_6H_4-(CH_2)_m-SH$, $m = 1-6$). This material is available free of charge via the Internet at http://pubs.acs.org.

LA0014050