



First-principles modeling of oligo(ethylene glycol)-terminated and amide group containing alkanethiolates

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Abstract

Recently, self-assemblies of $\text{HS}(\text{CH}_2)_{15}\text{CONH}(\text{CH}_2\text{CH}_2\text{O})_6\text{H}$ were found to undergo a reversible temperature-driven conformational transition from the helical to all-*trans* state [R. Valiokas, M. Östblom, S. Svedhem, S.C.T. Svensson, B. Liedberg 104 (2000) 7565]. The transition reveals distinctive signatures in the reflection–absorption (RA) spectrum associated with different conformations of the OEG portion of the SAM [R. Valiokas, M. Östblom, S. Svedhem, S.C.T. Svensson, B. Liedberg 104 (2000) 7565]. Here we report an extensive ab initio modeling of infrared RA spectra of molecular constituents of OEG-terminated amide-containing SAMs. The model spectra for this type of molecules (with large OEG and alkyl portions) are obtained, for the first time, by using DFT methods with gradient corrections. The position and relative intensities of all characteristic bands, observed in the fingerprint region of the SAM RA spectrum, are shown to be well reproduced by the single-molecule model spectrum calculated for a certain relative orientation of the alkyl- and OEG portions and the amide bridge. This provides us additional information about actual structure, particularly, molecular orientation within the OEG-containing SAMs in focus.

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1. Introduction

Self-assembled monolayers (SAMs) consisting of long-chain organic molecules chemisorbed on a suitable substrate provide new tools for controlling wetting, adhesion, lubrication and corrosion of surfaces and interfaces [2]. SAMs of oligo(ethylene

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glycol) (OEG)-terminated alkanethiolates (those which possess flexibility, abilities to modifications, high ordering, good structural control) represent a promising molecular material for biotechnological and medical applications. The use of OEG-terminated SAMs in studies of protein adsorption on organic surfaces was first demonstrated by Whitesides and co-workers [3]. Grunze and co-workers [4] have shown that SAM OEG moieties can exist in different conformations, and have related the ability to resist protein adsorption to the OEG conformation. Vanderah et al. developed a series of structurally well-defined OEG-SAMs on gold, where the SH group was attached to the OEG terminus rather than to the alkyl terminus [5], as well as highly ordered SAMs of methyl-terminated 1-thiaoligo(ethylene glycols) on gold [6].

In the current communication, we address a class of OEG-terminated SAMs on Au(1 1 1) supporting surfaces, which has been studied recently by means of standard and temperature-programmed infrared RA spectroscopy [1,7]. Specifically, we focus at the molecular geometry and orientation within a self-assembled monolayer of $\text{HS}(\text{CH}_2)_{15}\text{CONH}(\text{CH}_2\text{CH}_2\text{O})_6\text{H}$ molecules (EG₆-SAM). Structural details of OEG-terminated SAMs, such as orientation of alkyl and OEG portions of molecular SAM constituents, are rather guessed than known. To provide some quantitative grounds for understanding the SAM structure, we compare model RA spectra, obtained from all-electron ab initio geometry, vibration frequencies, and transition dipole moments (TDMs) for a single molecular constituent, with respective experimental data. The subsequent analysis shows that the model and observed RA spectra agree well only for a very restricted range of molecular orientations, giving us the likely position of SAM building blocks relative to the substrate surface.

2. Molecular orientation

In OEG-terminated SAMs that are composed of complex molecular aggregates of different molecular fragments, it is of prime interest to know the relative position of respective fragments. In our study, these are $(\text{CH}_2)_{15}$ —alkyl chain, CONH—amide group, and $(\text{CH}_2\text{CH}_2\text{O})_6$ = EG₆—hexa(ethylene glycol) chain. The orientation of alkyl and ethylene glycol chains is

determined by two sets of three Euler angles. The first one, tilt angle θ_A , azimuthal angle φ_A , and twisting angle ψ_A , specifies orientation of alkyl CCC plane with respect to the substrate surface. The tilt angle θ_A is an angle of tilting of z_A axis, i.e., the angle between z_A and the normal to the substrate surface n , while angle of rotation ψ_A is an angle of rotation of the $x_A z_A$ plane about the z_A axis. The axes x_A , y_A , and z_A are introduced in a commonly accepted way with the standard definition of azimuthal angle φ_A [8], see Fig. 1a. The second set of Euler angles, θ_E , φ_E , and ψ_E , gives spatial position of OEG part of the molecule. For the all-*trans* conformation of OEG chain (which was found experimentally in shorter OEG SAMs in silver [4a] and gold [1]), these angles determine the orientation of COC plane and their definition (in the $x_E y_E z_E$ frame of reference) is the same as that of θ_A , φ_A , and ψ_A with respect to CCC plane. For the helical OEG conformation, which is the actual molecular geometry EG₆-SAM at room temperature [1,7], the coordinate axes x_E , y_E , and z_E are defined as follows. Axis x_E coincides with the bisector of the angle formed by the first COC group of OEG chain (this is one of the twofold axes for PEO intersecting the helix axis at right angle [9]); orientation

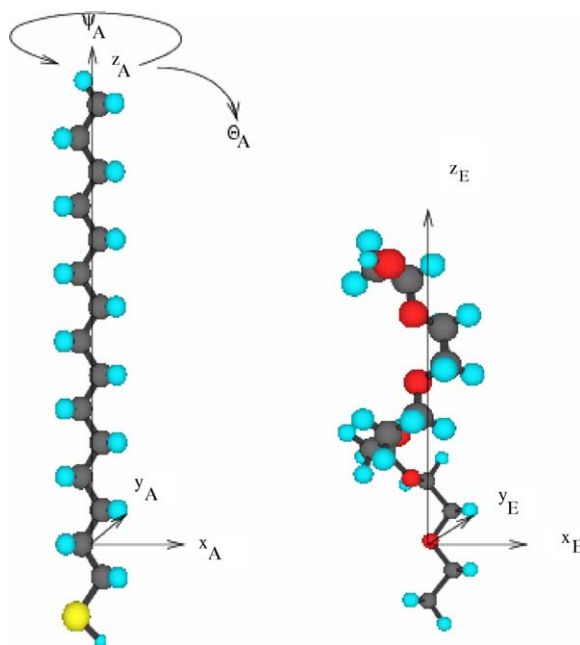


Fig. 1. Definition of (x_A, y_A, z_A) axes for alkyl segment (a), and (x_E, y_E, z_E) axes for OEG helix (b). Molecules are shown in the position, where all angles $(\theta_A, \varphi_A, \psi_A$ and $\theta_E, \varphi_E, \psi_E)$ are zero.

of axis z_E is given by the vector product of x_E and the bisector of the angle formed by the next, second, COC group; finally, axis $y_E = (z_E \times x_E)$, see Fig. 1b. The angles θ_E , φ_E , and ψ_E are determined by the transformation matrix from the $x_A y_A z_A$ to the $x_E y_E z_E$ system of coordinates, provided the alkyl chain orientation is known [10]. Hence, when the geometry optimization of the whole molecule is completed, one can find the orientation of the OEG portion for the given orientation of alkyl portion of the molecule.

3. Geometry optimization and molecular orientation within the SAM

The optimized geometry and TDMs of vibrational modes, which have been used here for modeling of infrared RA spectrum of specifically oriented $\text{HS}(\text{CH}_2)_{15}\text{CONH}(\text{CH}_2\text{CH}_2\text{O})_6\text{H}$ molecule, were calculated by using the DFT method with BP86 exchange-correlation functional (with 6-31G* basis set) as provided by the Gaussian-03 suite of programs (see [11] and references therein for details of the method). Since the intermolecular (mostly Van der Waals) interaction is relatively weak, the molecular geometry obtained by this DFT method yields a reasonable zero-approximation structure of SAM constituents. In helical conformation, the length of the whole molecule excluding S–H bond is equal to 38.6 Å. If the tilt angle of the alkyl segment θ_A , which is commonly evaluated to be in the range between $\sim 20^\circ$ and $\sim 30^\circ$ [4,8,12], is set 26° , and if we take into account the known distance between sulfur atom and the surface (1.9 Å [13]), the predicted SAM thickness is 38.9 Å. This is within the experimental errors of measured (ellipsometric) thickness 39.8 ± 1.7 Å [14].

To deduce the molecular orientation within EG₆-SAMs, we rely on the following experimental data. It has been established (see, e.g. [7]) that only a combined C–N–H bending and C–N stretching vibration (amide II) appears in the RA spectrum, while amide I vibration (C=O stretching) is nearly inactive. This implies (because of the “metal surface selection rule”) that the angle between the C=O bond and the substrate–surface normal n $\gamma_{\text{C=O}} \sim 90^\circ$ and the angle between C–N bond and n (that we will denote as $\gamma_{\text{C–N}}$) should be sufficiently small to give a large TDM normal component of amide II vibration. Furthermore,

a distinctive shift of the amide II mode has been revealed in [7]. It suggests that the overall lateral interaction within the SAM contains a contribution from the hydrogen bonding between neighboring amide groups. To allow the hydrogen bond formation, there should be the H and O atoms (which belong to nearest-neighbor CONH groups) at a distance close to 2 Å. Note that the properties just mentioned are specific for amide-containing SAMs. These strongly restrict the number of possible molecular orientations within the SAM that makes the present modeling especially instructive for establishing the SAM structure parameters, providing at the same time a good check of suitability of the usage of single-molecule geometry and orientation. Finally, the relative intensity of the symmetric and asymmetric bands, which correspond to CH-stretching vibrations¹ of the alkyl chain, is strongly dependent on the orientation of CCC plane. Hence, this is another requirement to be met in modeling of EG₆-SAM structure, as well as that in general, the choice of molecular geometry and orientation have to be consistent with observed infrared RA spectra of OEG-terminated alkanethiolates.

4. Model RA spectrum and associated SAM structure

To model the spectrum for a given molecular orientation with respect to the substrate surface, the output TDMs were recalculated to obtain the TDM components in the molecular coordinates, where z -axis coincides with z_A . Model spectra were obtained in the dipole approximation, as the sum of Lorentzian-shaped peaks, each centred at the fundamental mode frequency and having the half-width at half-maximum 5 cm^{-1} ; the peak height is proportional to the squared TDMs z component of the corresponding mode. It is worth emphasizing that in the presented results, neither frequency scaling nor fitting of relative peak intensity has been used.

Clearly, in the single-molecule approximation and under the given (ab initio optimized) geometry, the shape of RA spectrum depends only on the values of

¹ Symmetric and asymmetric with respect to the bisector of the HCH angle.

θ_A and ψ_A angles. As already mentioned above, the observed intensity of the symmetric and asymmetric bands which are due to alkyl CH_2 -stretching vibrations, sets a rather narrow range for these angles. These bands are very similar in their appearance in infrared RA spectra of self-assemblies of both OEG-terminated alkanethiolates [1,4,7] and pure alkanethiolates [8,12]. Therefore, experimental spectra of both kinds of SAMs have been used for comparison with calculated spectra, to ensure the validity of our modeling. Further, from a range of possible values of θ_A and ψ_A giving a reasonable agreement with experimental RA spectra in the CH_2 -stretching region (not shown here), the most likely molecular orientation was determined from the condition of the best fit of model and observed spectra in the fingerprint region. Then, the values of $\gamma_{\text{C=O}}$ and $\gamma_{\text{C-N}}$ angles were checked. As a result of the above-outlined analysis, which rests on the assumption that the actual molecular structure within the SAM can be modeled by the optimized single-molecule geometry, we have concluded that the whole molecule within EG₆-SAMs should be tilted by $\theta_A = 26^\circ$ and rotated by $\psi_A = -62^\circ$.

The corresponding model RA spectrum in the fingerprint region is compared with the experimental spectrum [1] in Fig. 2, where the molecule itself, for the values of θ_A and ψ_A indicated above, and

$\varphi_A = 288^\circ$, is depicted in the right-hand side of the figure. It is seen that the simulated spectrum, which does not contain any adjustable parameters, reproduces quite well the relative position and intensity of all significant features of the measured RA spectrum [1], which is offset for clarity. The assignment of fundamental OEG modes in the fingerprint region is well known [1,4–7]: asymmetric COC stretching + CH_2 rocking modes (963 cm^{-1}), asymmetric COC stretching modes (1114 cm^{-1}), CH_2 twisting modes (1244 cm^{-1}), CH_2 wagging modes (1349 cm^{-1}), and CH_2 bending modes (1464 cm^{-1}). The same assignment and very close to the experiment frequency values (see Fig. 2) are obtained in these calculations.

The apparent coincidence of a number of characteristic details between the measured and calculated spectra (demonstrated here for the first time) strongly support the validity of the given approach (see Fig. 2). In particular, in both spectra, one can see a pronounced asymmetry of the dominating peak in the region of interest. Usually, the high-frequency shoulder is attributed to the presence of non-helical conformational states in the OEG-SAMs, since amorphous and all-*trans* OEGs are expected to absorb in the region $1125\text{--}1150\text{ cm}^{-1}$ [1,4,6]. Our calculations give an alternative explanation to the shoulder due to a tilted orientation of the helical axis, see below.

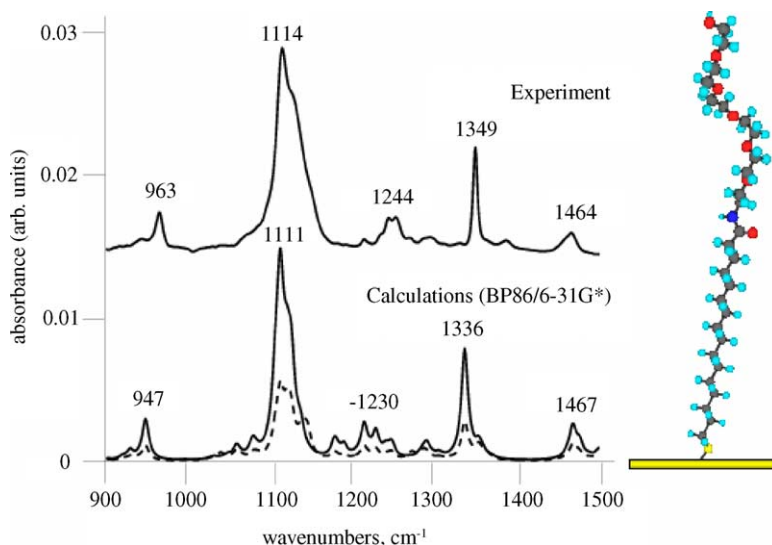


Fig. 2. Upper curve: measured spectrum of EG₆-SAM [1]; lower curves: calculated spectrum of oriented ($\theta_A = 26^\circ$, $\psi_A = -62^\circ$, solid line) and randomly oriented (dashed line) HS(CH₂)₁₅CONH-EG₆ molecules. Right-hand side: optimized geometry of HS(CH₂)₁₅CONH-EG₆ molecule for which $\theta_A = 26^\circ$, $\psi_A = -62^\circ$, $\varphi_A = 288^\circ$.

From the obtained molecular geometry and deduced values of θ_A and ψ_A follow the other EG₆-SAM structure parameters. The angles between the substrate normal and C=O and C–N bonds are $\gamma_{C=O} = 96^\circ$ and $\gamma_{C-N} = 27^\circ$. These values ensure a much larger apparent intensity of amide II vibration compared to amide I vibration. The minimal distance between the oxygen atom from one of the CONH groups within the SAM and the hydrogen atom of the nearest-neighbor amide group is realized at azimuthal angle $\varphi_A = 48^\circ$ (or $\varphi_A = 48^\circ + n \times 60^\circ$, $n = 0, 1, \dots$). This gives a hydrogen bond length equal to 2.5 Å, assuming that sulfur atoms on Au(111) form a $(\sqrt{3} \times \sqrt{3})R30^\circ$ hexagonal lattice and are separated from each other by 5 Å.

Thus, the BP86 optimized geometry suggests the following orientation of the SAM constituents: tilt angle $\theta_A = 26^\circ$, rotation angle $\psi_A = -62^\circ$, and azimuthal angle $\varphi_A = 48^\circ + n \times 60^\circ$. Then, spatial orientation of OEG part of the molecule is given by $\theta_E = 22.0^\circ$, $\psi_E = 24.5^\circ$, and $\varphi_E = -25.6^\circ + n \times 60^\circ$. A frequently accepted model aligns the OEG helix (z_E) axis within OEG-terminated SAMs with the normal to the substrate surface [4–6]. However, there is no direct experimental and/or theoretical proof that supports such an alignment. On the other hand, the substantial tilt of z_E axis θ_E predicted by this modeling allows us to give a plausible explanation for the above-mentioned shoulder at 1114 cm^{-1} : it is a contribution from vibrational modes with large TDMs in the x , y directions that become visible only due to a noticeable tilt of the helix axis. This is illustrated by comparing the lower solid line in Fig. 2 with dashed line that models the spectrum of randomly oriented HS(CH₂)₁₅CONH-EG₆ molecules. Similar arguments in favor of non-parallel orientation of helix axis with respect to the surface normal can be inferred from analysis of spectroscopic data obtained for the CH₂-stretching region [11].

In conclusion, the relative orientation within self-assemblies of HS(CH₂)₁₅CONH-EG₆ molecules on Au(111) substrate are deduced in a quantitative manner from comparison of ab initio modeled and observed RA spectra. Our modeling suggests that the alkyl CCC plane is tilted by $\theta_A = 26^\circ$ and rotated by $\psi_A = -62^\circ$ and $\varphi_A = 48^\circ$ (with a standard definition of the angles [8]). These angles demonstrate an impressive agreement between experimental and

non-fitted spectra in the fingerprint region, and give reasonable spacing between the nearest-neighbor amide groups that is consistent with hydrogen bonding. Other important parameters of the SAM structure are found to be as follows: amide bonds/substrate normal angles $\gamma_{C=O} = 96^\circ$ (amide I vibration is not seen in RA spectra) and $\gamma_{C-N} = 27^\circ$ (amide II vibration gives an intense band in RA spectra); the length of expected hydrogen bonding is 2.5 Å; the OEG helix tilt $\theta_E = 22.0^\circ$ and rotations $\psi_E = 24.5^\circ$ and $\varphi_E = -25.6^\circ$, see Fig. 1b. The obtained values can be helpful for realistic modeling a number of interesting properties and functional potentials of OEG-terminated SAMs. Applications of these data along these lines are currently under development.

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