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

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Abstract

Recently, self-assemblies of $HS(CH_2)_{15}CONH(CH_2CH_2O)_6H$ 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 $HS(CH_2)_{15}CONH(CH_2CH_2O)_6H$ molecules (EG_6-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 $(CH_2)_{15}$—alkyl chain, CONH—amide group, and $(CH_2CH_2O)_6 = EG_6$—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_Az_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 $x_Ey_Ez_E$ 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 EG_6-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

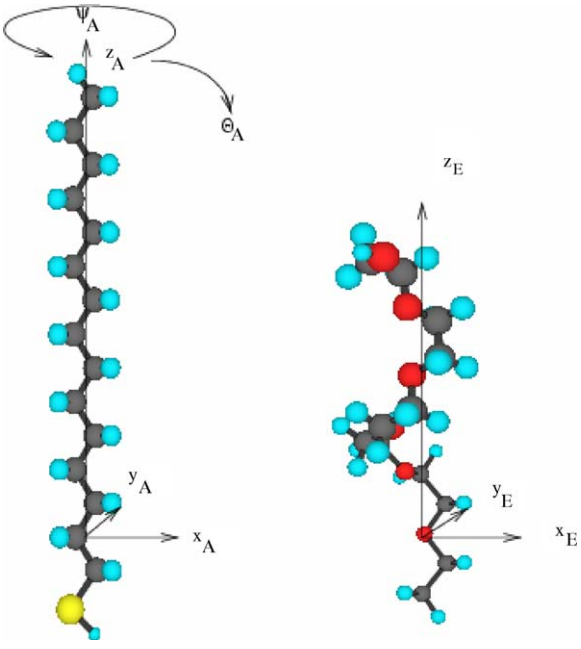

Fig. 1. Definition of (x_A, y_A, z_A) axes for alkyl segment (a), and (x_E, y_E, z_E) axes for OEG helix (b). Molecules are shown in the position, where all angles (θ_A, φ_A, ψ_A and θ_E, φ_E, ψ_E) are zero.