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Orientations of Chain Axes and Transition Moments in Langmuir–Blodgett Monolayers Determined by Polarized FTIR-ATR Spectroscopy

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FTIR–ATR dichroic ratios with and without a rotation of the ATR plates were measured for calcium or cadmium or lead stearate LB monomolecular films on germanium, hydrophilic silicon, and hydrophobic silicon plates. Various models for uniaxial or biaxial orientations of chain axes and transition moments are presented and critically evaluated. A biaxial orientation distribution was observed for calcium stearate. The average tilt and azimuthal angles of the chain axes were found to be 36° and 42°, respectively. Those angles of the transition moments of the CH_2 group were 66° and 46°, respectively. Cadmium and lead stearate monolayers had nearly uniaxial chain and moment distributions. Molecular orientations varied substantially with the ion type bound to the polar groups but little with the substrate surface. The average tilt angle of the chain axes was ca. 11° higher in X-type monolayers (methyl groups on the substrate surface) than in Z-type monolayers (polar groups on the surface) of lead stearate. The dichroic ratio for the cadmium stearate monolayer decreased from 0.98 at 25 °C to 0.84 at 130 °C. Recrystallization of the monolayer upon cooling was observed to be reversible and showed no time lag.

Introduction

Organized molecular films such as Langmuir–Blodgett (LB) multilayers and self-assembled monolayers have been investigated extensively over the past decade. Recently, electronic and photonic properties of these thin organic films have received much attention.[1,2] When molecules are highly oriented, their macroscopic properties can be quite different from those of unoriented bulk materials.

Fourier transform infrared (FTIR) spectroscopy is an excellent tool for studying the orientation of thin organic films at the molecular level, since it is nondestructive and highly sensitive. For molecular orientation determination, various modes of IR have been used, such as reflection–absorption (RA),[3–8] transmission,[4,9,10] attenuated total reflection (ATR),[11] with either unpolarized or polarized infrared beams. Frequently, combinations of results of several modes have been used. In many previous quantitative analyses, absorbance intensities or integrated absorbances have been interpreted by uniaxial moment orientation models, in which it has been assumed that transition moments are uniaxially distributed around the direction normal to the film surface.[12–21]

The combination of RA and transmission modes of IR spectroscopy[14–16,22–26] has been frequently employed, because these two modes are effective in differentiating transition moments lying parallel (or close to parallel) to the film surface from those normal (or close to normal) to that surface. It should be noted, however, that sample films must be prepared on a specular metallic surface for the IR–RA mode and on another nonabsorbing substrate for the IR transmission mode. Previous studies have ignored the effect of the substrate surface on the molecular orientation or assumed that it is the same. Furthermore, for monomolecular films the signal-to-noise (S/N) ratios of the RA and transmission modes are often too low to allow precise determination of orientation.

FTIR–ATR has much higher S/N ratios than the above modes.[27] Fundamental theories on IR spectroscopy through internal reflection elements (IRE) were developed by Harrick,[28–30] Zbinden,[31] and others.[32–42] The dichroic ratio, which is the key parameter used in determining the molecular orientations, is defined as the ratio of the absorbance intensity (or integrated absorbance) of s-polarized light (normal to the plane-of-incidence) to that of p-polarized light (parallel to the plane-of-incidence).[28,31] Ulman et al.[12,13] have applied a uniaxial moment model to self-assembled monolayers in order to find average tilt angles of transition moments ($\bar{\gamma}_0^M$) from the surface normal. Then, using the transition moments of the CH_2 group stretching vibrations, which are perpendicular to the molecular chain axis (for trans chains), they obtained an average tilt angle of the chain axes ($\bar{\gamma}_0$) by the following relation: $\bar{\gamma}_0 = 90° - \bar{\gamma}_0^M$. This relation is, however, strictly valid only for identically oriented molecules, and it is not generally valid, as will be discussed later. A different uniaxial model focusing on the chain axis was applied to lipid and peptide cast films[43] and LB films.[44,45] Biaxial models were also adopted for thin polymeric films.[46,47] Recently, the most detailed orientation description for an organic single crystal was used for rigid-rod oligoimide LB films.[48] In the previous studies, no systematic criteria for discriminating between possible orientation distributions were used.

New criteria based on rigorous FTIR–ATR spectroscopic theory are proposed in this study, to help choose proper orientation models for various LB monolayers prepared on semiconductor substrates. Orientations of both transition moments and chain axes are determined independently and are used for examining several previous models and for obtaining novel orientation information. The relations proposed in the previous studies are tested both theoretically and experimentally. The effects of the substrate surface, the metal ion type, and the temperature on molecular orientations in LB monolayers of salts of stearic acid are reported.

Theory of Orientation Evaluation by Polarized FTIR-ATR Spectroscopy

General Theory. The orientations of transition dipole moments and molecular chain axes are determined by[31] (1) transforming the vectorial transition moment (M) from a molecular (chain) coordinate system into a laboratory frame and (2) calculating the projection (or coupling) of the moment M on (or with) the electric field (E) of the radiation at the surface of an IRE (here, we use the 45°-cut trapezoid ATR plate).

The molecular crystallographic coordinates (*a*, *b*, and *c* axes) and the laboratory cartesian coordinates (*x*, *y*, and *z* axes) are shown in Figure 1. The *z* axis is along the normal to the film or to the ATR surface; the *x* axis is along the propagation direction of the IR beam; the *y* axis is along the direction of the s polarization. The p polarization lies in the O*xz* plane (the plane-of-incidence), at 45° with each of the two axes. In this description, one presumes that a chain axis which can represent molecular orientations can be defined. An example is an all-trans chain in a crystalline film. In highly disordered systems, or gauche conformations, defining a chain axis is not useful, and then one describes orientations of transition moments directly. The polar angles are defined as follows: γ is the tilt angle of the molecular chain axis (*c* axis) from the surface normal (*z* axis); ϕ is the azimuthal angle, the one between the *c′* axis and the *x* axis; Θ is the angle of the transition moment M with the *c* axis; and θ is the third Eulerian angle between the O*zc′* plane and M_p, which is the projection of M onto the plane (the circle in Figure 1b) normal to the *c* axis, as depicted in Figure 1c. The transformation equations of the molecular coordinates of M into the laboratory

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