Optically Induced Band Shifts in Infrared Spectra of Mixed Self-assembled Monolayers of Biphenyl Thiols

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Optically induced band shifts in reflection absorption infrared spectra (RAIR) of mixed self-assembled monolayers (SAMs) are reported. SAMs of 4-trifluoromethyl-4-mercaptobiphenyl dispersed in 4'-methyl-4-mercaptopiphenyl on gold exhibit significant shifts of the spectral envelope of the symmetric CF$_3$ stretch and the b$_{1u}$ skeletal mode. A linear relationship is observed between the band positions, the band intensity, and the surface CF$_3$ group concentration. To rationalize the observed changes in band positions and shapes, a classical electromagnetic theory approach is used, providing an excellent agreement between theory and experiments. The simplified RAIR signature of 4'-trifluoromethyl-4-mercaptopiphenyl on gold is a unique example of the surface selection rule.

Introduction

While self-assembled monolayers (SAMs) of alkane-thiols on gold are one of the most thoroughly studied systems, thiophenolate SAMs have only recently attracted attention. This new class of SAMs offers the following advantages. First, biphenyl thiolates are rigid and planar molecules, making these SAMs simple, yet ideal model systems to investigate surface phenomena. Second, chemical derivatization provides a simple means to change the electron density distribution in the molecule (e.g., its dipole moment). Third, 4-mercaptopiphenyl derivatives are readily available materials.

We have been using alkane thiolate SAMs as model surfaces to study wetting, adhesion, and friction and for surface-initiated ionic polymerization.

Although many analytical techniques afford information on the elemental composition of surfacerlayers, vibrational spectroscopy is unsurpassed in elucidating the nature, structure, and orientation of molecules at interfaces. The application of RAIR spectroscopy in surface analysis revealed many details of the molecular structure and will continue to play an important role in developing a comprehensive understanding of the nature of thin organic films.

The chemical and structural analysis of RAIR spectra often relies on comparison with bulk spectra. Significant changes of the intensity contour of RAIR spectra compared to transmission spectra occur as a function of the refractive index of the material and the substrate as well as the orientation and packing of the molecules in the film. To distinguish the optical, chemical, and structural effects, a theory approach is necessary. The RAIR experiment can be described by the interaction of a light beam with a smooth reflective surface. The theory which relates the macroscopic variables of the experiment with the incident and reflected electric fields at the interface is based on the boundary value solutions of Maxwell’s equation for stratified media with uniform dielectric functions. The simplest case involves an isotropic adsorbate layer identi-
cal to a known bulk material on an ideally flat surface. The orientation of adsorbates, that is, the first moment of the orientation distribution, can be calculated from RAIR spectra because of the anisotropy of the interfacial wave field. The interference of the incident and reflected wave fields at grazing angles on a conducting substrate results in an enhanced electric field normal to the surface. Therefore, the intensity of a vibrational mode is, in general, given by the square of the scalar product of the electric field and the projection of the transition dipole moment on the surface normal. This is referred to as surface selection rules.\textsuperscript{21} If the optical functions of the substrate and the adsorbatase as the adsorbate layer thickness are available, it is, in principle, possible to compute the RAIR intensities as a function of orientation.\textsuperscript{22} A more complicated situation arises when the adsorbate is anisotropic but otherwise identical to the bulk material. In this case, the refractive index should be formulated as an optical tensor.\textsuperscript{23} Another problem in interpretation can be caused by surface roughness.\textsuperscript{24} If adsorption significantly renders the force constants, normal modes, and band shifts in mixed SAMs. To rationalize the observed gold. We report the first observation of optically induced RAIR spectra of 4′-trifluoromethyl-4-mercaptobiphenyl (1) and 4′-methyl-4-mercaptobiphenyl (2) mixed SAMs on gold. We report the first observation of optically induced band shifts in mixed SAMs. To rationalize the observed changes in band positions and shapes, a classical electromagnetic theory approach is used, providing excellent agreement between theory and experiments.

**Experimental Section**

**Substrates.** Gold substrates were prepared by evaporating gold on glass slides (Fisher), without any adhesion layer, according to a procedure published elsewhere.\textsuperscript{25}

**SAM Preparation.** SAMs and mixed SAMs of 1 and 2\textsuperscript{19} were prepared by adsorption from 10μM solutions in ethanol (for mixed SAMs the total concentration was 10μM). The thickness of all monolayers as estimated by ellipsometry was 13±1 Å, with almost no scattering of ellipsometric values throughout the sample. Adding contact angle test of water on all SAMs and mixed SAMs were essentially the same, 85±1°. Advancing methylene iodide (CH\textsubscript{2}I\textsubscript{2}) contact angles were 60±1° for 1 and 42±1° for 2. Contact angle hysteresis was in all cases, suggesting a uniform distribution of CF\textsubscript{3} and CH\textsubscript{3} groups. Monolayers stored under nitrogen, or in ethanol, for days showed no change in thickness and wettability.

**Fourier Transform Infrared Spectroscopy (FTIR).** Infrared spectra were recorded on a Nicolet 760 spectrometer with a SpectraTech 80° fixed resolution (2500 scans), using a SpectraTech 80° fixed resolution (2500 scans), using a SpectraTech 80° fixed resolution (2500 scans), using a SpectraTech 80° fixed resolution (2500 scans), using a SpectraTech 80° fixed resolution (2500 scans), using a SpectraTech 80° fixed resolution (2500 scans). RAIR spectra of 1 and 2 show a common band at 1033 cm\textsuperscript{-1}, assigned to a fundamental mode,\textsuperscript{26} of equal intensity. The integrated intensity of this band is the same for all spectra (within 5%), suggesting that mixed SAMs have essentially the same coverage and molecular orientation. The concentration of 1 in mixed monolayers was determined from the integrated intensity of the symmetric CF\textsubscript{3} (1327 cm\textsuperscript{-1})

\begin{equation}
\tilde{\mathbf{r}}(\nu) = \sqrt{n_{\nu}^2 + \frac{f(v_{0}^2 - v^2) - if \nu}{(v_{0}^2 - v^2)^2 + (\nu \Gamma)^2}}
\end{equation}

where \(n_{\nu}\) is the refractive index far away from the absorption band (1.4 for 1 and 2), \(f\) is the damping constant, \(\Gamma\) is the bandwidth, \(v_{0}\) is the peak position, and \(\nu\) stands for the wavenumber. On the basis of the IR spectrum of 1 in CCl\textsubscript{4}, the following parameters were found: \(v_{0}(\text{CCl}_{4}) = 1072\text{ cm}^{-1}, f(\text{CCl}_{4}) = 25,000\text{ cm}^{-1}\), \(\Gamma(\text{CCl}_{4}) = 3850\text{ cm}^{-1}\) and \(\nu_{0}(\text{CCl}_{4}) = 1327, \nu(\text{CCl}_{4} + \text{g}) = 63,000\text{ cm}^{-2}\), \(\Gamma(\text{CCl}_{4} + \text{g}) = 7\text{ cm}^{-1}\). A mixture of two noninteracting systems, the refractive index is equal to the sum of the contributions due to each substance, that is,

\begin{equation}
\tilde{\mathbf{r}}(\nu) = \tilde{\mathbf{r}}_{1}(\nu) + \tilde{\mathbf{r}}_{2}(\nu)(1 - \chi)
\end{equation}

Here, \(\chi\) is the molar fraction and \(\tilde{\mathbf{r}}_{1}(\nu)\) and \(\tilde{\mathbf{r}}_{2}(\nu)\) are the refractive indices of compounds 1 and 2. The refractive index of the underlying substrate was taken from the literature.\textsuperscript{27} Therefore, the intensity of a vibrational mode is, in general, given by the Fresnel equation:

\begin{equation}
R_{01/2} = \frac{R_{01} + R_{02} + 2Re[R_{01} R_{02} e^{2\nu_{01}(\nu)}]}{1 + R_{01} + R_{02} + 2Re[R_{01} R_{02} e^{2\nu_{01}(\nu)}]}
\end{equation}

R is the reflectance, \(r\) is the reflectance coefficient, \(R_{01}\) indicates the real part of the expression in parentheses, and \(d_{1}\) is the film thickness. The reflection coefficients at each interface are given by the Fresnel equation:

\begin{equation}
R_{0j} = \frac{\tilde{\mathbf{r}}_{j} \cos[\phi_{j}] - \tilde{\mathbf{r}}_{i} \cos[\phi_{i}]}{\tilde{\mathbf{r}}_{j} \cos[\phi_{j}] + \tilde{\mathbf{r}}_{i} \cos[\phi_{i}]}
\end{equation}

The angle of incidence in each medium is given by the Snell equation \(\tilde{\mathbf{r}}_{j} \sin[\phi_{j}] = \tilde{\mathbf{r}}_{i} \sin[\phi_{i}]\). The reflectance, \(R_{0j}\), equals the square modulus of the reflection coefficient. The phase factor \(\gamma_{2}\) of medium 1 is given by \(\gamma_{2} = 2\pi n_{2} \cos[\phi_{1}]\). Care must be taken to compute the proper sign of the phase factor.\textsuperscript{29} The RAIR absorbance is given by

\begin{equation}
A = -\log_{10} \frac{R_{1}^{*}}{R_{2}^{*}}
\end{equation}

where \(R_{1}\) is the reflectivity of the film–substrate interface and \(R_{2}\) is the reflectivity of the substrate (no film present). The free parameters are the film thickness (determined by ellipsometry) and the bandwidth (determined from RAIR spectra).

If the adsorbate molecules are oriented but otherwise identical to the bulk material, the intensities of each mode are scaled to the following condition:

\begin{equation}
A \propto |\tilde{\mu}|^{2} \tilde{\mathbf{r}}^{2} E^{2}
\end{equation}

where \(\tilde{\mu}\) is the surface normal, \(\tilde{\mu}^{*}\) is the transition dipole moment, and \(E\) is the electric field vector. The refractive index in the infrared is usually obtained from a randomly oriented bulk phase. As a result, alignment of the dipole moments of the adsorbate molecules gives an experimentally observed intensity for each mode of 3 times that for the calculated isotropic spectrum. This

\begin{itemize}
\item [\textsuperscript{22}]Allara, D. L.; Nuzzo, R. G. Langmuir \textbf{1985}, 1, 52.
\item [\textsuperscript{25}]The slides were baked at 300 °C in a vacuum oven. A thickness of 1000 Å of gold was evaporated at a deposition rate of 1.5–2 Ås\textsuperscript{-1} at 300 °C and the samples were annealed at this temperature for 18 h. Imaging with atomic force microscopy (Digital Instruments Nanoscope III) revealed plateaus of up to 5000 Å diameter. Putnam, A.; Blackford, M. H.; Jerico, M. H.; Watanabe, M. O. Surf. Sci. \textbf{1989}, 217, 276, 76.
\end{itemize}
IR Spectra of Mixed SAMs of Biphenyl Thiol s

![Image](https://example.com/image.png)

Figure 1. Comparison of the transmission infrared spectra of 1 in the solid (top, KBr pellet) and the liquid (bottom, CCl₄) state. The relative intensities and the width of the bands reflect sensitively to the physical state of the material. The asterisk indicates bands of CCl₄.

Results and Discussion

Transmission Infrared Spectra and Mode Assignment. The infrared spectrum of 4′-trifluoromethyl-4-mercaptobiphenyl (1) can be rationalized if the skeletal fundamental modes are assigned based on a model of symmetry D₂h, according to which the CF₃ groups are assumed to be points, and to add to these the fundamental modes of the C₆H₆ groups.²⁶ Compound 1 shows unusually strong bands in the mid infrared region. The band contours and the relative intensities react sensitively to the physical state of the material. The IR spectrum of 1 dissolved in a liquid shows narrow, resolved bands, whereas a solid dispersion of 1 shows broad bands (Figure 1). Because of the strong permanent dipole moment of the CF₃ moiety and of the molecule as a whole due to the electron donor and acceptor properties of the SH and CF₃ substitutents, as well as possible π-stacking interactions of the aromatics, strong molecular interactions are expected. The random nature of such interactions is expected to increase the bandwidth through lifetime broadening, vibrational coupling, and other inhomogeneous broadening mechanisms. In dilute solution, molecular interactions are diminished by the surrounding solvent. The translational and rotational motions may fluctuate more rapidly, resulting in motional narrowing of the bands.²⁵ The relevant peak positions and assignments for compound 1 are summarized in Table 1.

Reflection–Absorption IR Spectra. SAM of 1. The RAIR spectrum of a SAM of 1 shows two striking features (Figure 2). First, the intensity contour is dramatically simplified, and second, the band maxima are shifted to higher energy. On the basis of the discussion of the previous section, the transition dipole moments have the following directions (Table 1).

The transition dipole moments of the antisymmetric CF₃ stretching modes (1133 and 1170 cm⁻¹) are perpendicular to the molecular axis and in and out of the plane defined by the aromatic rings (x-y direction). The complete absence of these two modes in the RAIR spectrum implies that the transition dipole moment of these modes must be oriented parallel to the surface. The transition dipole moment of the symmetric CF₃ (1327 cm⁻¹) and the δ₃b skeletal mode (1072 cm⁻¹) are in the direction of the molecular axis (z direction). The presence of these two modes (1072 cm⁻¹) implies that the transition dipole moments are oriented normal to the surface. The symmetric CF₃ and the δ₃b skeletal mode are orthogonal to the antisymmetric CF₃ stretching modes. On the basis of the surface selection rule, there is only one possible explanation for the simplified signature of the RAIR spectrum: the molecules are almost exclusively oriented in the direction of the surface normal.³³ The bottom part of Figure 2 shows the calculated band intensities of the symmetric CF₃ and the skeletal mode for a monolayer based on the assumption of an upright orientation. The relative and absolute computed intensities are in excellent agreement with the experimental values.

A comparison with the infrared transmission data (Table 1) reveals that the symmetric CF₃ mode is shifted from 1327 cm⁻¹ (transmission) to 1340 cm⁻¹ (SAM) and the δ₃b skeletal mode is shifted from 1072 cm⁻¹ (transmission) to 1078 cm⁻¹ (SAM), respectively. The computed peak

<table>
<thead>
<tr>
<th>position (cm⁻¹)</th>
<th>intensity symmetry direction of μ</th>
<th>assignment</th>
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<tbody>
<tr>
<td>1072</td>
<td>vs</td>
<td>b₃b</td>
</tr>
<tr>
<td>1133</td>
<td>vvs</td>
<td>u + g</td>
</tr>
<tr>
<td>1170</td>
<td>vvs</td>
<td>u + g</td>
</tr>
<tr>
<td>1327</td>
<td>vvs</td>
<td>u + g</td>
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(33) This mode of orientation may require a 180° bond angle at the sulfur atom (sp³ hybridization). This is in agreement with our simulation results that the energy difference between sp³ and sp² hybridization at the sulfur atom is small. See: Sellers, H.; Ulman, A.; Shnidman, Y.; Eilers, J. E. J. Am. Chem. Soc. 1993, 115, 9389.
positions (1339 and 1078 cm$^{-1}$) are, again, in excellent agreement with the experimental values. An analysis of the origin of these peak shifts will be given in the next section.

Compared to the infrared spectra of 1 in the solid and the liquid state (Figure 1), the RAIR spectrum (Figure 2) coincides best with the solution spectra in terms of the general band contours and relative intensities. The intermolecular interactions present in the solid seem to be absent in the monolayers. Intuitively, one would expect molecular interactions to be diminished in oriented monolayer assemblies. This is supported by the noteworthy observation that the bandwidth of the symmetric CF$_3$ (7 cm$^{-1}$) and the b$_{uu}$ skeletal mode (5 cm$^{-1}$) is smaller in the monolayer than in the liquid state (10 and 6 cm$^{-1}$, respectively). Apparently, dissipative mechanisms operative on adsorbed species play only a minor role. For this reason, the refractive index of the adsorbates has been identified in the literature: (a) the blue shift due to mechanical renormalization, (b) chemical effects due to surface bonding, and (c) lateral interactions between neighboring oscillators (vibrational coupling). A change of force constants, normal modes, or charge distribution induced by (a) or (b) as a result of adsorption seems unlikely. One would expect this effect to be operative at all coverages which is not observed. In addition, the b$_{uu}$ fundamental mode at 1003 cm$^{-1}$, common for both compounds 1 and 2, remains constant in position and intensity for all concentrations (inset Figure 3).

Vibrational coupling effects (c) encompass both through-bond and through-space interactions of adjacent oscillators and cause a coverage-dependent frequency shift. It can be shown that the vibrational coupling constants are a function of the energy separation of the modes under consideration. Since the vibrational frequencies for 1 and 2 are widely separated, the coupling constants are negligible. The v$_u$(CF$_3$) and the b$_{uu}$ skeletal mode can be considered as isolated vibrations. As a result, mechanism (c) is of only minor importance. The model employed to compute the band contours does not take into account electronic or coupling effects. It considers the mixed monolayer as a thin film with an effective refractive index which is equal to the sum of the contributions due to each substance; the reflectance is computed from first electromagnetic principles (see Experimental Section for details). The excellent agreement of experimental and computed band contours suggests that the major effect is a purely optical one and that other mechanisms are of minor importance. It should be pointed out that we do not observe a concentration-dependent bandwidth or a change of relative intensities; on the contrary, the bandwidth and the peak intensity ratio ($\nu$(CF$_3$)/b$_{uu}$(skeletal mode)) remain constant ($2.77 \pm 0.1$). This is another indication for the absence of coupling mechanisms.

The assumption of using an effective refractive index equal to the sum of the contributions due to each substance requires that the mixture behaves like an ideal solution (no change of density and absence of strong molecular interactions). This is in agreement with the observation made above that molecular interactions in mixed monolayers are diminished. Contributions from anisotropy in these films are also negligible. The agreement of theory

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(35) For a general introduction, see: Bradshaw, A. M.; Schweizer, E. In Advances in Spectroscopy: Spectroscopy of Surfaces; Hester, R. E., Clark, R. J. H., Eds.; Wiley: New York, 1988; Vol. 16, pp 413–488 and references cited herein. The "self-image" shift causes a peak shift toward lower energy and can be ruled out as a principle mechanism.

and experiment with this simple model for the optical response function is indeed remarkable.

The peak shift can be understood as follows: Because of the standing wave field on a conducting substrate, the amount of radiation removed from the incident beam is governed by the reflectivity and absorptivity of the film–substrate interface. In a simplified analysis, the reflectance is attributed to the real part $n(\hat{\nu})$, while the absorptivity is connected with the imaginary $k(\nu)$ of the complex refractive index, $n(\nu)$. The strong anomalous dispersion of the modes under consideration results in an enhanced reflectivity (more light at the detector) at the low-energy side and a reduced reflectivity (less light at the detector) at the high-energy side of the band maxima, $v_s$. This results in an apparent shift of the band contour toward higher energy.  

Figure 4 shows the experimentally observed and computed band shifts (solid lines) and band intensities (peak value) of the two modes as a function of the $\text{CF}_3$ concentration in the mixed SAM. It should be noted that the extrapolation of the intensity to zero coverage (dotted line, 1327.6 and 1072.7 cm$^{-1}$) is equal to the peak positions of the liquid sample (1327 and 1072 cm$^{-1}$). These two findings indicate that, first, all molecules contribute equally to the intensity and, second, that domain formation in mixed SAMs can be ruled out.  

The simultaneous close agreement of calculated and experimentally observed peak positions and peak intensities as a function of composition validates our approach. The simultaneous close agreement of calculated and experimentally observed peak positions and peak intensities as a function of composition validates our approach. 

Experimentally, our approach is in a sense validated by this simultaneous agreement.

Conclusions

We present a unique example of the surface selection rules: 4′-trifluoromethyl-4-mercaptobiphenyl (1) forms self-assembled monolayers in which the molecules are oriented in the direction of the surface normal. This result is directly inferred from the complete absence of the antisymmetric modes of the $\text{CF}_3$ group in the RAlR spectrum of 1. The transition dipole moments of these modes are perpendicular to the molecular axis.

For the first time, we report optically induced peak shifts in mixed self-assembled monolayers of 4′-trifluoromethyl-4-mercaptobiphenyl (1) and 4′-methyl-4-mercaptobiphenyl (2). We demonstrate that peak shifts are caused by optical effects as a result of the strong anomalous dispersion of the modes. To compute the reflectance of the thin film interface, the optical response function of mixed SAMs is approximated by an isotropic effective refractive index equal to the sum of contributions from each component. The simultaneous close agreement of calculated and experimentally observed peak positions and peak intensities as a function of composition validates our approach.

Our analysis shows that the orientation of the transition dipole moments remains the same in pure and mixed SAMs. From a comparison of transmission IR spectra and RAlR spectra, we infer that molecular interactions in SAMs, such as $\pi$-stacking or dipolar interactions, are diminished as one would expect for oriented monolayer assemblies.

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References

2. Patches of analyte with an approximate size of the employed wavelength would create coherent wave fronts; as a result, refraction and reflection occur as governed by the optical constants of the pure analyte. Such a sample would show a constant peak position independent of concentration.