Inter- and Intramolecular Temperature-Dependent Vibrational Perturbations of Alkanethiol Self-Assembled Monolayers

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The infrared spectra of octanethiol, dodecanethiol, and hexadecanethiol (C₈, C₁₂, and C₁₆, respectively) monolayers adsorbed on Au(111) textured surfaces have been explored in the 25–300 K regime. The C–H stretching modes typically shift by several wavenumbers to lower frequencies and the intensities increase by as much as 75% as the temperature is decreased, providing evidence of, among other effects, the coupling of these stretching modes with lower energy vibrational modes. In contrast, for all temperatures below 300 K, the positions of the C–H bands of fully hydrogenated C₁₆ shift by several wavenumbers to *higher* frequencies as the hydrogenated adsorbates are increasingly diluted in a matrix of fully deuterated C₁₆, showing that all bands are subject to intermolecular couplings. The analysis of the behavior of the C–H stretching bands suggests that the temperature dependence of the vibrational frequencies associated with the methylene stretching modes is principally due to intermolecular couplings, whereas the temperature dependence of the vibrations associated with the methyl terminations is largely due to intramolecular couplings. It is suggested that the highly constrained geometry of the isotopically diluted monolayer may provide an environment that is less sensitive to intramolecular couplings with low-frequency modes than that of urea–clathrate-isolated species.

Introduction

Quantitative infrared spectroscopy of the C-H stretching bands is widely used for the characterization of condensed acyl chains including polymers, lipid membranes, and self-assembled monolayers. Ideally, such a characterization would include information on both the molecular conformations and the orientation of the molecular system within the macroscopic sample under investigation. For relatively simple film constituents containing extended hydrocarbon chains, the position and the width of C-H stretching bands are often used to probe chain order and identify structural phase transitions; for these components, it is commonly presumed that the spectroscopic signature of a highly ordered film is the observation of the dominant methylene stretching bands at relatively low frequencies. The origin of this is the presumed reduced density of conformational (gauche) defects in such films, because gauche defects tend to have vibrational frequencies several wavenumbers higher than the all-trans conformations.¹ In the special case of highly organized films on planar surfaces, the intensities can be analyzed in terms of average molecular orientations relative to the polarization vector of the incident radiation field, according to standard dipole selection rules.^{2,3} Although the computational implementation of these principles may be complex (according to the sophistication of the treatment of the substrate's optical response), the conceptual simplicity of these principles makes the use of quantitative infrared spectroscopy very appealing in surface science.

Self-assembled monolayers (SAMs) of simple organic species chemically bound to noble metal surfaces have been explored extensively using this approach, and many of the structural models were initially developed on the basis of these spectral studies. In the case of the organothiol monolayers adsorbed on

Au(111) surfaces, Parikh and Allara's² formalism to study thin films is commonly applied. It is based on the decomposition of an appropriate reference spectrum (usually taken to be the isolated molecule or microcrystal in an inert host matrix) into individual bands with known orientations of the individual transition dipole moments relative to the molecular axis, and then the optical equations for these optical properties and those of the substrate for various model structures are resolved. The parameters that define this structural model (e.g., molecular tilt and twist, which define the projection the individual transition dipole moments onto the incident radiation field) are systematically varied to optimize the agreement with the experimental IR-RAS data. Clearly, the appropriate reference spectrum is the key ingredient for this approach, and the authors caution that there can be "no significant difference with regard to inter- and intramolecular interactions, electronic structure and packing density between the reference and film phase".² In the case of the bulk polymethylene chains, these interactions have been characterized in great detail by Snyder et al. and MacPhail et al.;⁴⁻⁶ intramolecular couplings take the form of Fermi resonances between the fundamental stretching modes and combinations of the chain bending modes. Intermolecular couplings can be evidenced by comparing the bulk *n*-alkane spectra with those of the same species isolated within the 5.25 Å diameter cylindrical pores of urea-clathrates;⁷ these intermolecular interactions are caused by the resonant interaction of oriented and identical oscillators among adjacent molecules and have been explored in detail for simple adsorbates such as CO adsorbed on crystalline copper surfaces.⁸⁻¹⁰ To our knowledge, however, there is little information available in the literature concerning these effects in SAM systems, and as such, the structural parameters extracted from these measurements and analyses may include systematic errors. This lack of information is due, in part, to the much lower signal-to-noise ratio in the monolayer films as compared to the bulk samples.

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The interpretation of the spectral properties of these films is becoming increasingly important as the study of SAMs extends into new regimes of temperature and molecular environments, and notwithstanding the experimental challenges, it is increasingly important to understand the underlying factors that determine the band positions and intensities for the monolayer systems. Infrared spectroscopy has been used by Nuzzo et al.¹¹ to characterize the temperature-dependent behavior of long-chain alkanethiol monolayers on gold. They concluded that most of the important changes observed in the low-temperature infrared spectra reflected an intrinsic dependence of the C-H stretching modes and the elimination of gauche defects near the chain terminations; large scale reorientation of the molecules was not deemed to be a significant factor, due to the already optimized geometry of the two-dimensional SAM system. This was supported by qualitatively similar observations on crystalline *n*-alkanes by Snyder and co-workers.⁶ Bensebaa et al.¹ have confirmed that the increased band intensities that are observed upon heating of n-alkanethiol SAMs above 300 K are due to the introduction of such defects, thus supporting the interpretation of the cryogenic results. However, recent molecular dynamics simulations suggest that alkanethiol SAMs can undergo temperature-dependent structural transitions by the variation of tilt angles^{12,13} or orientation angles.¹⁴ Experimental validation of these theoretical works by infrared spectroscopy requires a quantitative understanding of the intrinsic behavior of the C-H stretching bands as a function of both the temperature and chemical environment.

One of the objectives of the present work is to explore interand intramolecular interactions in SAMs, to better understand the nature of the IR-RAS results for alkanethiol SAMs. Isotopic dilution is a very simple method to isolate intramolecular and resonant intermolecular coupling contributions in vibrationnal spectra without significant structural perturbations. To clarify the temperature-dependent vibrational behavior of alkanethiol SAMs on gold, we have monitored the band intensities and positions as a function of temperature for pure and isotopically diluted hexadecanethiol SAMs. The type of analysis employed herein is predicated upon the assumption that there is no preferential aggregation of one isotopic species within the chemisorbed film (i.e., that the h_{33} -C₁₆ and d_{33} -C₁₆ film constituents are perfectly miscible in the two-dimensional adsorbed state). Indeed, it has been suggested that mixed Langmuir-Blodgett films may show compressive behavior that is distinguishable from that of the isotopically pure films, but the origins of these differences were not elaborated. Although it is difficult to directly probe this issue, Buckingham et al.¹⁵ have shown that the onset for isotope-based segregation in melts of linear C_n molecules is expected only for chains containing at least 100 methylene repeat units; above this threshold, the nonequivalent chain folding dynamics may lead to phase separation, depending on the temperature. Segregation was presumed to be negligible in the work on three-dimensional mixtures of hydrogenated and deuterated C₃₂, and ideal mixing behavior was considered to be operant. According to Buckingham's analysis, phase separation of three-dimensional h_{33} -C₁₆ and d_{33} -C₁₆ may be possible for temperatures below 2 K, and as such, we conclude that this process is not relevant to the present study. Furthermore, it should be noted that if twodimensional segregation of the h_{33} -C₁₆ and d_{33} -C₁₆ components of the film occurred, the local environment of each component would more closely resemble a pure film and would mask any composition-dependent effects; the observed compositiondependent spectra can only underestimate the actual degree of intermolecular couplings.

This study shows that the spectral positions and intensities of the h_{33} -C₁₆ components of the SAM provide evidence of interand intramolecular couplings, and we have isolated the relative magnitudes of these effects; we also make preliminary suggestions as to the fundamental nature of these couplings. This work shows that the direct use of CH2-derived band positions to assess the density of gauche molecular defects in SAMs confounds the spectroscopic influence of local gauche effects with longrange compositional disorder, as both tend to broaden the observed band envelopes and displace them to higher frequencies. Similar conclusions were obtained by Kodati et al.¹⁶ for condensed phase acyl chains, but as will be shown, the environment and behavior of the two-dimensional SAM vary considerably from those of the three-dimensional condensed phases. We feel that the demonstration of these effects may have a significant impact on the use of quantitative infrared spectroscopy to elucidate the structural characteristics of these C_n SAMs. It has been noted² that this structure-only approach cannot simultaneously fit the intensities of the observed CH₃ and CH2 associated bands, and local film defects were suggested to be the underlying cause. Parikh and Allara's initial work² applied the protocol to the case of C₁₈ SAM bound to a polycrystalline Au(111) substrate, using the spectrum of C₁₉H₃₉-CO₂Na as a reference; in their optimized geometry it was found that the bands associated with the methyl terminations could not be satisfactorily explained on the basis of an all-trans molecular model, and structural disorder near these groups was proposed to be the fundamental cause.

As mentioned above, this approach to the structural analysis of the film using grazing incidence reflection-absorption spectroscopy^{2,3,17} presumes that the reflectivity of the monolayer/ substrate system is determined by the absorption band strengths of the isolated molecules (as measured in an inert host matrix such as KBr), subject to the structural perturbations imposed by the highly oriented film system and the projection of the transition dipole moments of the C-H oscillators onto the surface normal (plus the optical perturbation introduced by the substrate and the index of refraction of the film). This structural model explains, for example, the high absorption of the symmetric methyl stretch bands (r⁺, 2875 cm⁻¹) in the twodimensional environment of the film, where the transition dipole moment is almost parallel to the surface normal) as compared to the isotropic melt^{5,16} and in the case of alkanethiol-coated gold nanoparticles.^{18,19} However, the neglect of intermolecular effects when considering the band strengths and band positions may lead to systematic errors in the structural parameters extracted from these measurements. The present work provides an alternative basis to understand these discrepancies in terms of differing intermolecular couplings related to the various vibrational modes of the alkanethiol SAM.

Experimental Section

The Au films were evaporated on freshly cleaved mica surfaces following a modification of DeRose's protocol,²⁰ which is known to prepare high-quality films with a strongly Au(111) texture. Mica substrates (Proscience-Techniglass ASTM-V2) were degassed at 300 °C for 12–20 h in a turbomolecularly pumped system ($\sim 1 \times 10^{-7}$ Torr) prior to deposition. Following evaporative deposition of ~ 150 nm of gold, the samples were annealed at 300 °C for 2 h under vacuum prior to removal from the system. When possible, the gold substrates were immediately exposed to the thiol solutions; otherwise, they were stored in sealed polycarbonate vials under an argon atmosphere until use.

Octanethiol, dodecanethiol, and hexadecanethiol $(h_{17}-C_8)$, h_{25} -C₁₂, and h_{33} -C₁₆, respectively) were used as received (Aldrich, 95%). Deuterated hexadecanethiol (d_{33} -C₁₆) was synthesized from palmitic- d_{31} acid (Cambridge Isotope Laboratories, 98%) following a slight modification of Badia's protocol.¹⁹ d_{31} -Palmitic acid (0.5 g, 1.7 mmol) was reduced with LiAlD₄ (Aldrich) (0.47 g, 14 mmol) in freshly distilled tetrahydrofuran to the corresponding alcohol (0.46 g, 98% yield). d_{33} -Hexadecanol was then treated under reflux with 30 mL of 48% HBr, giving the d_{33} -bromohexadecane (0.47 g, 83% yield). Finally, the d_{33} -bromohexadecane was treated with Na₂S₂O₃ (0.37 g, 1.5 mmol) in ethanol under reflux, and the resulting Bunte salt was hydrolyzed with 4 mL of concentrated HCl to give the desired d_{33} -hexadecanethiol (0.37 g, 94% yield) after purification by flash chromatography. The overall yield of the synthesis is 75%, and the purity of the final product was >99%as found by GC-MS. Film deposition onto the Au/mica substrates was by immersion in 1.0 mM thiol/methanol solutions for at least 24 h. For the (h,d) mixed monolayers, the deposition solutions were prepared from appropriate volumes of the pure 1.0 mM h_{33} -C₁₆ and d_{33} -C₁₆ solutions. Individual 10 × 25 mm SAM/Au/mica samples were secured to 3 mm thick copper carrier plates using copper straps to provide thermal contact to the front-surface gold film. These carrier plates had a 10×5 mm tab extension in the plane of the sample to provide a thermal contact to the sample manipulator and cryostat assembly. With the carrier plates and the attached samples lying in the vertical plane, and mechanically supported on two rearward-facing protrusions, this tab loosely fit into a Ga-filled "well" on the copper sample support block that was permanently attached to an XYZ-tilt-rotation manipulator (Thermionics). A 25 W heater is integrated into the sample support block as well. OFHC copper braids connected the sample support to the tip of a closed-cycle He cryostat head (APD Cryogenics model 21-B) to permit sample movement. This sample support block was electrically and thermally isolated from the 300 K manipulator support using glass beads as the tilt pivot points; electrical insulation from the grounded cryostat was via a sapphire plate sandwiched between OFHC plates. When the sample was cooled to below the freezing point of Ga (27 °C), the Ga provided a rigid link between the sample carrier plate and the manipulator system, as well as an excellent thermal link to the cryostat; the vapor pressure of Ga is always below 10⁻¹¹ Torr in the temperature range employed herein.21 Temperatures were measured and stabilized using a 0.07% Fe/Au thermocouple attached to the sample support and a commercial controller system (Omega Engineering CYC-3000). Due to the relatively large thermal mass of the carrier plate plus sample support assembly, the maximum heating and cooling rates were 10 and 1.4 K/min, respectively; at such slow rates of temperature variations, there is no evidence that the SAM is out of thermal equilibrium or that a significant temperature gradient exists between the thermocouple and the organic film. No spectroscopic evidence of contamination by adsorbed species was found upon cooling or during the multihour experiments.

Samples were transferred via a turbopumped load-lock into our in-house-designed vacuum system (240 L/s TNB-X ion pump, base pressure of 2×10^{-10} Torr at ambient temperature, 5×10^{-11} Torr with cryostat operating) and mounted onto the sample stage using a UHV-wobble-stick.

Spectra were recorded by focusing the modulated infrared radiation from a Nicolet Magna-IR 560 bench (ThermoInstruments) onto the surface using an external parabolic mirror assembly and planar steering optics and collecting the reflected

TABLE 1: Observed Bands for Pure h_{33} -C₁₆ and d_{33} -C₁₆ SAMs

	transition dipole	C-H position (cm ⁻¹)		C-D position (cm ⁻¹)	
band	orientation	25 K	300 K	25 K	300 K
d ⁺	in C−C−C plane ⊥ to molecular axis	2848	2851	2093	2097
d ⁻	\perp to C-C-C plane	2921	2921	2197	2198
r^+	to terminal \hat{C} -C	2876	2878	~ 2078	~ 2078
r ⁻ a	in C−C−C plane ⊥ to terminal C−C	2962	2962	2217 ^a	2217 ^a
r ⁻ _b	\perp to C-C-C plane \perp to terminal C-C	2955	~2957		

^{*a*} r $^{-}_{a,b}$ for d_{33} -C₁₆ are unresolved at all temperatures studied.

beam using an ellipsoidal mirror configured with one focus at the sample and the other at the 1.0 mm² InSb detector element. The incident angle is $\sim 85^{\circ}$ from the surface normal.^{3,17} Light was transferred into and from the vacuum system via differentially pumped NaCl windows.²² For reasons not related to the work presented herein, the optical path is folded within the vacuum system using two plane-mirrors that can be independently adjusted. These data are collected without the use of a polarizer, such that the overall intensities are systematically a factor of 2 lower than in works that include the polarizer. Data were collected with a stated resolution of 2 cm^{-1} (post-FFT data point spacing of 1.0 cm^{-1}) with a 3 cm/s moving mirror velocity, Happ-Ganzel apodization, and no zero-filling. "Absorption spectra" present the reflectivity of a SAM referenced to that of a pristine Au/mica surface, whereas " Δ absorbance spectra" present the reflectivity referenced to the same film measured at 300 K. With the exception of baseline correction at 2800 and 3000 cm⁻¹ (2050 and 2250 cm⁻¹ for the d_{33} -C₁₆ results), no data editing or filtering has been performed on the data used in this study. All measurements were repeated at least in triplicate using different samples; the error bars reflect the sample-to-sample variations. Peak heights and positions are determined using in-house LabVIEW-based software.

Spectroscopic Background

The nomenclature used in this work to identify the C–H and C–D stretching modes follows that commonly used in spectroscopic studies of C_n films. Table 1 shows the band assignments for these bands, along with the description of the transition dipole vector direction (presuming an all-trans C_n chain conformation) and the band positions measured for a pure h_{33} -C₁₆ and a pure d_{33} -C₁₆ film at 300 and 25 K. The projections of these transition dipole moments onto the surface normal (and therefore to a first approximation the observed intensities) as a function of molecular tilt and twist angles have been elaborated elsewhere.²³ In the following text we will identify the samples using the notation x%- C_n , where C_n identifies the chain length and x identifies the percentage of the fully hydrogenated C_n chains in the film.

Results

Figure 1 shows the effect of sample temperature on the C–H stretching vibrations of a 100% h_{33} -C₁₆ monolayer; the top panel (A) presents the absorption spectra of the films, whereas the lower panel (B) presents the Δ absorbance spectra, the latter focusing on the details of the temperature-related *changes*. The most evident temperature effect on the spectra is the progressive intensity increase of the principal absorption bands upon cooling, along with a shift of the peaks to lower frequency. Large



Figure 1. Temperature-dependent direct absorbance spectra (A) and Δ absorbance spectra (B) of 100% h_{33} -C₁₆ SAMs; sample temperatures are 300, 250, 200, 150, 100, 50, and 25 K. The Δ absorbance spectra are obtained using the 300 K reflectivity as a reference.

intensity increases and spectral shifts have also been observed by Nuzzo et al.¹¹ and by Bensebaa et al.¹ for h_{45} -C₂₂ films cooled to 80 and 155 K, respectively. These changes are fully reversible on heating from 25 to 300 K and upon subsequent thermal cycles. There is no evidence of discontinuous spectral tendencies that could be indicative of first-order phase transitions within the film. It is noteworthy that in all cases there remain significant spectral changes as the temperature is cooled to below 200 K, at which temperature molecular dynamics simulations indicate that the population of structural gauche defects in the film is below 0.3%.24 Thus, structural changes are most likely restricted to minor changes in molecular orientations rather than chain conformations. Indeed, tilt-angle changes of 2-4° have been predicted for the sub-200 K regime,²⁴ as have azimuthal rotations of molecular domains with respect to the substrate.¹⁴ Figure 2 presents the absorption and Δ absorption spectra for pure d_{33} -C₁₆ films in the 25-300 K regime, using the same scales as Figure 1 for pure h_{33} -C₁₆; to the best of our knowledge these are the first published spectra of d₃₃-C₁₆ SAMs and their temperature dependencies. The C-D stretching bands are of significantly lower intensity than their C-H counterparts, and their evolution with temperature is less pronounced. This has been reported previously for bulk n-alkane samples and for *n*-alkanes trapped within urea-clathrates.^{7,16} Like their hydrogenated analogues, the dominant C-D stretches shift by several wavenumbers to lower frequencies and increase in intensity as the temperature is reduced to 25 K. However, the relatively poor signal-to-noise ratio of the C-D monolayer spectra makes the quantitiative analysis less certain; instead, this work will concentrate on the behavior of the d⁺ and r⁺ C-H bands as the film composition is changed.

Figure 1 shows that the growth of the d⁺ band (~2850 cm⁻¹) is caused by increased optical absorbance at progressively lower frequencies, such that the overall envelope is subject to a systematic red shift. In our measurements of h_{17} -C₈, h_{25} -C₁₂, and h_{33} -C₁₆, the d⁺ band presents the strongest increase of peak absorbance, whereas previous work on h_{45} -C₂₂ films^{1,11} showed more pronounced changes on the d⁻ structure (~2929 cm⁻¹). Figure 3A shows that the d⁺ band shifts linearly from ~2851 to 2848.5 cm⁻¹ as the temperature is reduced from 300 to 25 K (9.1 × 10⁻³ cm⁻¹/K); h_{25} -C₁₂ presents similar trends. The d⁺ intensity (Figure 3B) increases sublinearly with reduced tem-



Figure 2. Temperature-dependent direct absorbance spectra (A) and Δ absorbance spectra (B) of 100% d_{33} -C₁₆ SAMs; sample temperatures are 300, 250, 200, 150, 100, 50, and 25 K. The Δ absorbance spectra are obtained using the 300 K reflectivity as a reference.



Figure 3. Peak position (A) and peak absorbance (B) for the symmetric methylene stretching vibration (d^+) of 100% h_{33} -C₁₆ and h_{25} -C₁₂ samples as a function of sample temperature. The straight lines of (A) and the curves of (B) are provided to guide the eye through the data.

perature in the T = 25-300 K regime for all chain lengths, with the magnitude of the increases being systematically greater for the longer chain systems. The d⁺ peak approaches an asymptotic intensity of ~1.1 mAbs for h_{33} -C₁₆. The integrated intensity grows (relative to that at 300 K) by 75%. The r⁺ bands shows similar behavior (Figure 4): increased absorptions at progressively lower frequencies than the peak position at 300 K cause the peaks to shift almost linearly from 2877.5 to 2876 $\rm cm^{-1}$ (5.5 × 10⁻³ cm⁻¹/K). The r⁺ intensity increases sublinearly as the temperature is reduced to 25 K, with integrated intensity changes of $\sim 30\%$ relative to that at 300 K. The behavior of the r⁺ peak is relatively insensitive to the chain length. There is some evidence of a net loss of intensity of the background near the r⁺ peak (Figure 1B), but the integrated area of this loss is significantly less than the net growth of the vibrational band; as such, the observed increase is not simply the redistribution of oscillator strength. The temperaturedependent evolutions of the asymmetric bands (i.e., d⁻ and r⁻) are more difficult to establish. The methylene-derived d⁻ peak



Figure 4. Peak position (A) and peak absorbance (B) for the symmetric methyl stretching vibration (r^+) of 100% h_{33} -C₁₆ and h_{25} -C₁₂ samples as a function of sample temperature. The lines are provided to guide the eye through the data.

shows a rather uniform growth across the entire absorption feature (Figure 1B) down to 200 K. At lower temperatures, the difference spectra show a distinct splitting into a peak at 2919 cm⁻¹ and a smaller, sharper component at 2922 cm⁻¹, indicating the presence of two overlapping spectral bands. The resolution of this splitting is highly dependent upon the quality of the SAM; surfaces that exhibit broader than usual CH₂ bands do not exhibit this splitting. The integrated intensity of the d⁻ band (2910-2930 cm⁻¹) grows by ~45% in the 300-25 K regime. As reported by Nuzzo et al.,¹¹ the r⁻ bands show a complex behavior with temperature. The out-of-plane stretch r⁻_b becomes a resolved peak at \sim 250 K, then increases in intensity and shifts by -2.0 cm^{-1} with lower temperatures. At low temperatures the $r_b^{\,-}$ band is dominant; the results of Nuzzo et al. for 100% h_{45} -C₂₂ show similar trends, although the resolution of the two antisymmetric components is less evident in their data. These workers attributed the evolution of the CH2- and CH3-derived bands to the reduction in the number of gauche defects near the chain terminations and the stabilization of a structural unit cell containing more than one molecule at low temperatures;¹¹ it was also proposed that the intensity increases may reflect intrinsic changes of the vibrational modes, rather than changes to the structural characteristics of the film. This is supported by the similarity to the spectroscopy of crystalline polymethylene samples.⁶ To distinguish the structural from the spectral properties of these films, we have repeated the thermal cycling experiments with mixed monolayers containing controlled proportions of h_{33} -C₁₆ and d_{33} -C₁₆. With the increasing isotopic dilution of the SAMS, these bands suffer shifts to higher frequencies and are subject to intensity changes; the magnitudes, but not the direction of the spectral shifts, are influenced by the temperature. Panels A and B of Figure 5 show the position and the intensity, respectively, of the d^+ band for T = 300 and 25 K for the five film compositions considered; the shifts and intensity changes are monotonic functions of temperature in the sub-300 K regime. In addition to the \sim 3 cm⁻¹ downward shift that has been described upon cooling for pure films, the symmetric methylene band can shift as much as 4 cm^{-1} to higher frequencies as the h_{33} -C₁₆ molecules are increasingly diluted in a d_{33} -C₁₆ film; the effect of this dilution is more significant at lower temperatures. Remarkably, the peak position



Figure 5. Peak position (A) and peak absorbance (B) for the symmetric methylene stretching vibration (d^+) of h_{33} -C₁₆ samples as a function of the SAM composition, for sample temperatures of 25 and 300 K. The curved lines are provided to guide the eye through the data.

converges toward 2852.5 \pm 0.3 cm⁻¹ in the limit of the isolated h_{33} -C₁₆ molecule, regardless of the sample temperature; expressed in a slightly different manner, the position of the symmetric methylene band of an isolated h_{33} - C_{16} impurity in a d_{33} - C_{16} film is essentially independent of temperature below 300 K. Under these conditions any intramolecular interactions that influence the d⁺ band position have no significant temperature dependence. Given that intramolecular interactions are expected to be largely independent of film composition, we anticipate that the intramolecular interactions within a 100% h_{33} -C₁₆ SAM should also be subject to negligible temperature-induced d⁺ band shifts. This strongly suggests that essentially all of the 3 cm⁻¹ downward shift of this band for the full SAM that is seen upon cooling (Figure 3A) is due to changes in the intermolecular couplings, with very little intramolecular contributions. We stress that all evidence indicates that the physical environment of this impurity molecule is identical to that of the 100% h_{33} -C₁₆ film. Figure 5B shows that the intensity of the d^+ peak is a linear function of the quantity of adsorbed h_{33} -C₁₆; as required, the optical absorbance of the film tends toward zero as the number of absorbers is decreased, and the optical absorbance per molecule (at a given temperature) is independent of film composition, showing that intermolecular effects are minimal. The apparent optical absorbance of the d⁺ band increases at lower temperatures, as anticipated from Figures 1 and 3, with a d⁺(300 K)/d⁺(25 K) ratio of 0.6–0.7 for all film compositions. Whereas the d⁺ band *position* is influenced by changes in the intermolecular interactions with temperature, the variation of the d⁺ band *intensity* with temperature is determined almost exclusively by changes in the intramolecular couplings.

The behavior of the r⁺ bands with changing composition is fundamentally different from that of the d⁺ band. Figure 6A shows that the r⁺ band shifts by $\sim 2 \text{ cm}^{-1}$ to higher frequencies as the hydrogenated fraction of the film is reduced from 100 to 0%, revealing the influence of changing intermolecular interactions. The magnitude of this shift is, to our experimental precision, insensitive to the sample temperature; equivalently, the 2.0 cm⁻¹ temperature-induced downward shift of the r⁺ band is independent of the film composition. For the reasons discussed above in the context of the d⁺ band, we anticipate that the intramolecular contributions are largely independent of film



Figure 6. Peak position (A) and peak absorbance (B) for the symmetric methyl stretching vibration (r^+) of h_{33} -C₁₆ samples as a function of the SAM composition, for sample temperatures of 25 and 300 K. The curved lines are provided to guide the eye through the data, whereas the straight lines are obtained by linear regression fits to the most dilute data available in this study.

composition and, therefore, virtually all of the 2.0 cm^{-1} temperature-induced shift seen for the r⁺ band in the 100% h_{33} - C_{16} SAM (Figure 3A) is due to changes in the intramolecular couplings, with very little that can be attributed to changes in the intermolecular couplings. Although the r^+ band position is affected by both composition and temperature (changing intermolecular and intramolecular couplings, respectively) to similar degrees, these two influences are completely uncoupled. We note that the observed linear trends of the peak position provide confirmation that there is no significant isotopic segregation in the film, because segregation would tend to maintain the peak frequency to be that of the pure h_{33} -C₁₆ film, regardless of composition. Figure 6B demonstrates that the intensity of the C-H r⁺ band varies nonlinearly with the h_{33} -C₁₆ content of the film; as expected, the intensity tends to zero at low h_{33} -C₁₆ compositions, but films that are rich in the hydrogenated component have greater intensities than would be predicted on the basis of the isolated molecule spectrum. Note that these data were obtained with the same samples as the d⁺ bands of Figure 5, which displayed linear intensity-composition trends; the observed nonlinearity of Figure 6B cannot be due to surface compositions that do not reflect that of the prepared thiol/ methanol deposition solutions or manipulation errors. It is clear that the nonlinearity of Figure 6B will have important consequences for attempts to interpret the intensity of the r⁺ band of a two-dimensional SAM on the basis of the optical properties of isolated molecules or attempts to correlate depletions of this band to changes in the film composition upon reaction or substitution at random sites.²⁵ The dotted lines of Figure 6B shows the extrapolated r⁺ intensities based on the most dilute samples used in this study at 25 and 300 K. For the 100% h_{33} -C₁₆ SAM, we estimate that the intermolecular interactions can increase the r^+ intensity by as much as 40–50%. It is interesting to note that the $r^+(300 \text{ K})/r^+(25 \text{ K})$ ratio is a constant 0.6 for all samples. The insensitivity of this ratio to the film composition (and its close correspondence to the ratio calculated for the d⁺ band above) indicates that the temperature-induced variations of the r⁺ band intensity are largely due to changes among the intramolecular interactions.

Discussion

The results presented herein demonstrate clearly that although temperature-dependent structural changes are certainly expected in C_n/Au SAMs,²⁴ the infrared spectroscopic signatures of these films are also strongly affected by the molecular environment of the film for any given structural motif. The magnitude of these intermolecular effects can exceed that of the structure-induced effects, and as such, it is important to understand the physical basis for the various perturbations that are imposed upon the vibrational spectra of the films as the microscopic and macroscopic environments of the SAM are modified.

The key conclusions that are derived from this study are as follows:

(1) The d^+ band position is strongly influenced by both temperature and film composition; the temperature dependence is largely of *intermolecular* origin.

(2) The r^+ band position is influenced by both temperature and composition to similar degrees; the temperature dependence is largely of *intramolecular* origin.

(3) The d^+ band intensity (per molecule) is insensitive to the composition of the film; the temperature dependence is due to *intramolecular* interactions.

(4) The r^+ band intensity (per molecule) is strongly influenced by intermolecular interactions; the temperature dependence is largely of *intramolecular* origin.

The tendencies of the methylene stretching bands (d⁺, d⁻) toward isotopic dilution and temperature have been previously addressed for crystalline polymethylene chains^{5,6} and for condensed phase hexadecane and decane.¹⁶ They too observe a systematic shift of the d⁺ band to higher frequencies as the fraction of hydrogenated molecules is reduced; this was attributed to the perturbation of the intermolecular Fermi resonance,⁵ which couples the fundamental symmetric CH₂ stretching mode with lower frequency modes of the solid. Although this resonance affects the distribution of intensity among the various sub-bands related to methylene vibrations of the extended chains, it is not expected to significantly change the total integrated intensity of the fundamentals themselves.⁵ Because the d⁺ band at ~ 2850 cm⁻¹ is mostly constituted of the fundamental symmetric stretching of the CH₂ group and the secondary bands (2890 and 2853 cm^{-1 5}) are weak, the intensity of the principal d⁺ band (per molecule) should not be strongly affected by isotopic dilution. This is as observed in our study.

The d⁺ intensity loss with the increasing temperature has been also observed in the polymethylene chains in crystalline state,⁶ and it has been pointed out that density, refractive index, and conformational effects are too small to account for the large intensity changes. They proposed that most of the intensity changes are associated with the low-frequency large-amplitude "lattice-like" modes, especially the torsional modes of the carbon skeleton. These modes affect the transition dipole moment through higher order dipole-derivative terms. This explanation is highly consistent with our observations. First, this is a strong intramolecular effect, and the amplitudes of these low-frequency modes are temperature dependent, with higher temperatures leading to increased molecular flex, thus changing the coupling to the fundamental stretching mode. Although not considered in detail herein, this also explains the difference of intensity change among h_{17} -C₈, h_{25} -C₁₂, and h_{33} -C₁₆ because this disruption is more important in longer chains that can have larger amplitude low-frequency motions.

Low-frequency modes could also be a part the observed frequency shift of the d^+ band, because they induce a loss of symmetry required for the intermolecular Fermi resonance. Thus,

increased temperatures lower the intermolecular coupling, leading to a shift in frequency similar to isotopic dilution. Finally, the participation of low-frequency modes can explain the observation that the amplitudes of changes in both intensity and frequency with temperature are significantly lower in d_{33} - C_{16} SAMs as shown in Figure 2. Amplitudes of low-frequency modes are mass dependent and decrease in going to the perdeuterated chains.

It is interesting to compare the "isolated" molecule behavior obtained at infinite dilution in the SAM with that obtained by embedding similar length n-alkane chains in urea-clathrates.^{7,16} The cavities formed in these solids are \sim 5.25 Å in diameter and are therefore considerably larger than the \sim 4.5 Å cylindrical "diameter" of the all-trans conformation. In both cases it is presumed that intermolecular interactions have negligible importance due to the relatively large separation between identical molecules. Kodati et al.¹⁶ have shown that the d⁺ and d⁻ bands of C₁₆ in this environment shift to lower frequency with reduced temperature at a rate of $1.5 \times 10^{-2} \text{ cm}^{-1}/\text{K}$ and ascribed this to the intramolecular effects of chain vibrations as discussed above. In the present study, the d⁺ band shifts at infinite dilution (Figure 5A) are too small to be reliably measured, but they are certainly below $3 \times 10^{-3} \text{ cm}^{-1}/\text{K}$ (i.e., at least 4-fold lower). We suggest that this remarkable reduction in the sensitivity to low-frequency chain motion is due to the highly constrained environment of the C16 SAM, as compared to the extended pore structure of the clathrate. Snyder et al.⁷ have estimated that the expectation value of the torsional "flex" of C_{16} in urea-clathrates is ~0.58 rad². It is not possible for individual molecules that are chemisorbed to the Au(111) substrate to deform to this degree, and although the collective motion of large numbers of adjacent molecules may allow such distortions, this would be energetically prohibitive. By structurally confining the C₁₆ molecules in the two-dimensional SAM, low-frequency vibrations are sharply reduced, even at 300 K, such that the temperature dependence is less pronounced. This is consistent with recent STM²⁶ and molecular dynamics simulations¹² that indicate that even short-chain SAMs are essentially crystalline in nature, even at 300 K, contrary to previous reports.²⁷ One possible origin for the intermolecularbased shifts of the d⁺ peak with temperature seen in hydrogenrich films is dipolar coupling among adsorbates. This effect is most commonly observed as a repulsive interaction between transition dipole moments that are aligned perpendicular to the surface plane^{8-10,28} that leads to positive peak shifts, but attractive interactions have been reported due to transition dipole moments lying closer to the surface plane. We have confirmed that simple lattice sums of the transition dipole-transition dipole interaction of the d^+ and d^- modes within the organic layer provide attractive interactions for highly organized SAMs with tilt and twist angles of $\sim 30^{\circ}$ and $\pm 45^{\circ}$, although we are unable at this point to estimate the amplitude of this interaction or how it varies with temperature. We presume that as the dynamic motion of the chains is reduced, this attractive interaction causes the progressive shift of the d^+ band to lower frequencies as shown herein.

To our knowledge, this is the first report of the r^+ band behavior against temperature and dilution; this band is often obscured in the spectra of solid polymethylene by the d⁺ bands and is poorly resolved in h_{33} -C₁₆/d₃₃-C₁₆ mixtures.¹⁶ Our results show that the r⁺ and d⁺ bands show similar shifts to higher frequency with isotopic dilution. However, in the case of the r⁺ band the results presented herein indicate that changes of intramolecular couplings are the origin of the temperatureinduced shifts, whereas the d⁺ band position was more affected by intermolecular couplings. We suggest that the intramolecular nature of the r⁺ shifts is likely caused by the less constrained movement and flex of the methyl chain terminations in the SAM environment. Elimination of gauche defects near this site may have a role at elevated temperatures, but it is unlikely that there are sufficient numbers of such defects at lower temperatures that can still be removed; permanently trapped defect configurations cannot contribute to the observed temperature-induced shifts. It is interesting to note that intramolecular effects (related to the temperature-dependent fluctuations of the angular orientation of the methyl groups) have been invoked by MacPhail et al.29 to explain the splitting of the antisymmetric methyl stretches in *n*-alkane crystals. Although we have not explored this band in detail, it is interesting to note that this supports our conclusion that the spectral profile relating to the methyl terminations is largely affected by intramolecular interactions.

The nonlinearity of the r^+ intensity as a function of film composition is an issue that requires further work. Previous work has indicated that the IR-RAS intensity of the methyl modes is more difficult to reconcile with crystalline models of SAM structure², and it is important to determine if domain size effects are important.

Conclusions

This study has determined that both intra- and intermolecular factors have strong influences on the IR-RAS spectra of n-alkanethiol SAMs adsorbed on Au(111) surfaces. The relative contributions of these factors have been assessed using both temperature-dependent and composition-dependent IR-RAS spectroscopy. Although the temperature-dependent changes in the r⁺ and d⁺ band intensities are shown to be universally due to the changes in intramolecular couplings, the position of the d⁺ band evolves more profoundly with temperature due to changing intermolecular interactions. We propose that this may be due to intermolecular coupling of the transition dipole moments, which becomes more pronounced as the sample temperature is reduced and the h_{33} -C₁₆ content of the film increases. The temperature-related shift of the d⁺ bands at infinite dilution is significantly less than that of h_{33} -C₁₆ molecules trapped within urea-clathrate pores, indicating that the amplitude of the molecular distortions within these pores is larger than in the highly constrained two-dimensional SAM structure. Finally, we note that although the varying effects of inter- and intramolecular couplings on the spectra are quantifiable, their molecular interpretation requires more study; this would provide a more solid basis for the routine application of infrared spectroscopy to the structural study of these films.

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