

Surface-Mediated Segregation and Transport Processes in Mixed Hydrocarbon Multilayer Assemblies

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The transport and structural phase dynamics exhibited by multilayer assemblies comprised of cyclic and linear alkanes are analyzed with reflection absorption infrared (RAIR) and temperature-programmed desorption spectroscopies. Infrared spectroscopy reveals that methyl group substitutions have a significant effect on the nature of the mode softening seen in the C–H stretching region for surface-bound cyclohexanes. The magnitude of the red-shifts seen increases with the degree of methyl substitution. The energetics of the surface binding do not correlate in a simple way with the magnitude of red-shifts seen in the RAIR spectra, however. We find instead that the strengths of the surface interactions are more directly correlated with both the size and shape of the molecule (with the latter presumably reflecting its ability to form a densely packed structure). We also find that the diffusion of molecules in a mixed hydrocarbon multilayer assembly is weakly activated, with substantial interlayer mixing being seen at temperatures significantly below the threshold for the desorption of the multilayer. The mixing, while driven by mass action, shows a pronounced bias for the surface binding of *n*-alkanes over cycloalkanes of similar molecular weight (e.g., *n*-octane is more strongly bound on Pt(111) than is *cis*-1,3-dimethylcyclohexane). The data strongly suggest that attractive lateral interactions in the adsorbed layers lead to the biases seen in this surface-induced segregation. Thermal desorption spectra confirm this sensitivity and interestingly show multiple monolayer desorption features for cyclic alkane adsorbates when mixed in a monolayer assembly with an appropriate linear *n*-alkane. We suggest that the attractive lateral interactions in the monolayer lead to the formation of island domains and that the desorption kinetics appear to sensitively reflect this underlying rate/structure sensitivity.

Introduction

Hydrocarbon assemblies serve as extremely useful model materials for examining the nature of the phase and transport dynamics exhibited in more complex organic thin films. The structural and thermodynamic properties of one particular model system, thin films of the *n*-alkanes supported on Pt(111), have been described in detail by both this research group and others.^{1,2} In an earlier report, we described the nature of self-diffusion processes of *n*-alkane molecules bound in a self-similar series of (nominal) bilayer assemblies on a Pt(111) substrate. The present report extends this investigation, examining the transport rate–structure sensitivities evidenced in compositionally complex assemblies derived from mixtures of molecules with large structural or size differences (i.e., normal and cyclic alkanes). The fundamental properties of model thin-film materials of this sort—such as the nature of adsorbate–adsorbate and adsorbate–substrate interactions, the surface and interlayer self-diffusion, and the conformational dynamics of the adsorbate species—are critical to providing a better understanding of a number of important macroscopic phenomena of which adhesion,³ lubrication,^{4,5} surface-induced self-assembly,^{6,7} and catalysis serve as notable examples.⁸

The structures investigated here exhibit behaviors similar to those observed in other so-called two-dimensional mixtures.⁹

Such mixtures have been a focus of intense interest owing to the ease with which they lend themselves to the characterization of the thermodynamics of adsorbate–adsorbate and adsorbate–surface interactions.^{10,11} The systems most heavily studied to date comprise mixtures of monoatomic gases (e.g., Xe, Ar) or small organic adsorbates (e.g., CH₄, C₂H₆, etc.) physisorbed sequentially with total coverages varying from less than a full monolayer up to a multilayer. A variety of substrates have been employed in these investigations, although most work for reasons of experimental simplicity have used a nonmetallic material such as highly oriented pyrolytic graphite (HOPG).^{12–14} These studies have been reviewed by us in an earlier report,¹⁵ and only a few items of special interest to the context of the present work will be discussed here.

Of principal concern to the phase properties of any mixed adsorbate system is the issue of compatibility. Do the adsorbates phase-separate or form a solid solution? For the complex adsorbate structures examined here, what experimental methods might be used to shed light on such issues? The literature provides a useful background to consider these questions. Generally speaking, mixing behaviors are quite rare. For example, on graphite between 71 and 83 K,^{12–14} krypton and cyclohexane do not form a mixed adsorbed layer, but instead their sequential adsorption yields three-dimensional crystallites of the hydrocarbon as it is displaced from the surface by the rare gas. Theoretical models of this (and related) systems suggest that the most important factor in determining whether two

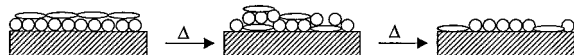
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adsorbates segregate or mix in an adlayer is the detailed balance between the various adsorbate–adsorbate and adsorbate–substrate interactions.^{9,16} For the Kr/C₆H₁₂ system, it is suggested that the driving force for displacement is the energy released when a dense krypton monolayer is formed.¹⁷

Studies of the adsorption of *n*-alkane chains from solution onto graphite^{18–21} offer further insights into the effects of a size/shape asymmetry on the phase properties of an adlayer structure. For example, molecular dynamics simulations of a solution formed by a long-chain hydrocarbon dissolved in benzene show a preferential segregation of the chains when confined between two graphite surfaces, and perhaps an induced ordering as well.²²

In this report, we present the results of a study that illustrates the nature of diffusion and adsorbate surface-segregation dynamics evidenced by model mixed hydrocarbon assemblies. Specifically, we examine the phase properties seen in bilayers formed by mixtures of normal and cyclic alkanes on Pt(111). Using temperature-programmed desorption (TPD) and reflection absorption infrared (RAIR) spectroscopies, we demonstrate the existence and nature of surface and interlayer transport phenomena that occur in these phases. We find that the adsorbate surface-segregation and transport processes are extremely sensitive to both size and molecular shape (i.e., that *n*-alkanes are more strongly retained at the surface than are cycloalkanes of similar size). The data suggest that the mechanism(s) of the exchange processes seen in the adlayer films involves a displacive equilibration of adsorbates, which in turn is based on the generation of free volume in the surface-contacting layer via conformational (and perhaps other) dynamics.

In the present work, we make extensive use of RAIR spectra to deduce information related to the segregation of species present in a multilayer assembly. The nature of this experiment is shown schematically below.



The starting sample, a thin-film superlattice, is easily prepared by sequentially dosing the crystal with a pair of adsorbates. Heating leads to a mass-action-driven evolution of the structure. The Pt(111) substrate is not an “innocent spectator” in this experiment. Of most interest in this work are the strong binding forces that occur with contacting segments in the physisorbed film and the substantial perturbations these interactions induce in the vibrational spectra of the $\nu_{\text{C-H}}$ oscillators. These effects are sufficiently dramatic as to allow, in conjunction with isotopic labeling studies, the average positions of an adsorbate to be followed during the thermal evolution of a thin-film assembly.

Experimental Method

Experiments were performed in ultrahigh vacuum using methods that have been described previously.²³ Only a brief overview is given here. Reflection adsorption infrared spectroscopic studies were performed in a stainless steel vacuum chamber equipped with turbomolecular, ion, and titanium sublimation pumps and having a base pressure of $<3.0 \times 10^{-10}$ Torr. The Pt(111) crystal was cleaned before each experiment by heating it in a 1.0×10^{-6} Torr atmosphere of dioxygen at 980 K for 5–8 min and subsequently annealing it at 1070 K or by Ar⁺ ion sputtering. In most experiments, sample dosing was performed in a manner similar to the “preadsorbed layer” technique described in the literature.²⁴ The exposures were made from the background and were calibrated (for the ion gauge sensitivity) by RAIRS and TPD. The Pt(111) crystal was cooled

to a temperature between the monolayer and the multilayer desorption temperatures for the specific hydrocarbon being studied. After exposure to the equivalent of several tens of monolayers at this temperature, a full coverage monolayer was obtained. In the transport studies, the monolayer dosing temperatures used for the various hydrocarbons studied are octane, 190 K; cyclooctane, 190 K; *cis*-1,3-dimethylcyclohexane, 200 K. After dosing, the pressure was allowed to recover before the crystal was cooled to 110 K, at which point subsequent components could be dosed and a multilayer formed. At this temperature, the partial pressure of the surface-bound component is negligible and the second component adsorbs only on the hydrocarbon precovered surface. The quantity of an adsorbate present in a mixed multilayer, irrespective of the location where it is bound, is referenced to that necessary to form a single monolayer of the adsorbate, θ_s .

To facilitate the differentiation of the two components in both infrared and desorption studies, fully deuterated *n*-octane was used to form either the preadsorbed or postadsorbed layer. The different frequencies of the various methyl and methylene C–H and C–D stretching modes, along with the significant perturbations of these modes that result from direct metal contacts, allow us to determine the orientations and relative positions of the hydrocarbons within the layers on the platinum surface. Furthermore, the desorption of each species can be independently monitored by TPD owing to the difference in the masses that obtain for the major cracking fragments. The specific ions followed were $m/e = 41$ for cyclooctane and $m/e = 50$ for the deuterated octane.

The alkanes, *n*-octane-*d*₁₈ (98+%), cyclooctane (99%), methyl cyclohexane (99%), and *cis*-1,3-dimethylcyclohexane (99%), were purchased from Aldrich, cyclohexane (98%) was purchased from EM Science, and *cis,cis,cis*-1,3,5-trimethylcyclohexane (99%) was purchased from Wiley Organics. All were degassed prior to use via the freeze–pump–thaw method.

RAIR spectra were taken with a Bio-Rad FTS-60A spectrophotometer aligned with *f*/15 optics at grazing incidence, 85° from the surface normal. A total of 1024 scans were coadded with a resolution of 4 cm^{−1}.

TPD spectra were obtained with a VG Quadrupole SXP 300 mass analyzer differentially pumped by a 60 L/s ion pump. The sample temperature and ramp rate were controlled by a Eurotherm temperature controller and a Lambda programmable power supply. Linear temperature program ramp rates of 2 K/s were used.

Results and Discussion

As noted above, the interaction of a hydrocarbon adsorbate with a Pt(111) surface leads to a significant perturbation of the normal modes of vibration.^{2,25} These significant effects provide a convenient and sensitive method for determining the organizational arrangement of the molecule in a thin-film assembly, especially with regard to whether the molecule is a surface-contacting species. The RAIR spectra of *n*-alkanes adsorbed on Pt(111) have been described and extensively reviewed elsewhere.^{2,15,25} In the present work, we consider systems that involve mixtures of an *n*-alkane with various cycloalkane adsorbates. The HREEL and RAIR spectra of the latter adsorbate class on Pt have received some attention in the literature.^{26–29} The descriptions given, though, do not cover all of the adsorbates used here or develop a sufficiently deep set of interpretations of the $\nu_{\text{C-H}}$ mode softening that accompanies their binding on Pt. We therefore present the results of a survey study of the RAIR spectra obtained in the C–H stretching region for several

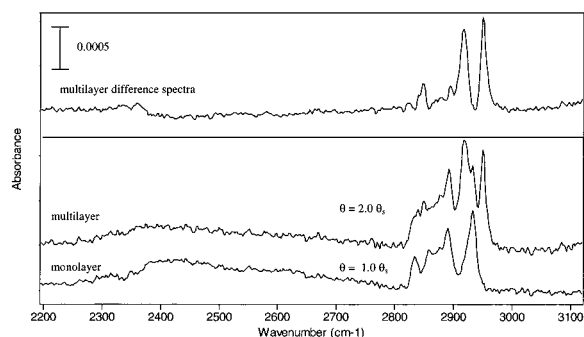


Figure 1. RAIR spectra of a *cis*-1,3-dimethylcyclohexane multilayer and monolayer on Pt(111). The lower panel shows absolute spectra for a monolayer and multilayer. The upper panel shows a multilayer difference spectrum.

cycloalkane adsorbates on Pt(111). The molecules studied include cyclohexane, methyl cyclohexane, *cis*-1,3-dimethylcyclohexane, *cis,cis,cis*-1,3,5-trimethylcyclohexane, and cyclooctane.

RAIR Spectra of Substituted Cyclohexanes on Pt(111).

Vibrational spectra of *cis*-1,3-dimethylcyclohexane in the C–H stretching region are shown in Figure 1 both for a monolayer and for higher multilayer coverages. The spectrum of the multilayer is presented in two forms. The bottom panel shows a spectrum of the multilayer measured at a coverage of $\theta \approx 2\theta_s$, where θ_s is the coverage found for a well-formed monolayer at saturation. For purposes of comparison, a spectrum of the monolayer (also obtained at $\theta \approx \theta_s$) is shown in this panel. A difference spectrum of the multilayer (computed against a monolayer rather than a clean surface single-beam reference spectrum) is shown in the upper panel of the figure. This latter method of presentation largely removes the contributions due to the surface-contacting segments.³⁰ It can be seen immediately from a casual inspection that the modes of the molecule seen in these spectra differ substantially depending on whether the molecules experience direct M···H–C contacts. In the monolayer spectrum, distinct features due to C–H stretching motions are observed between 2800 and 3000 cm^{-1} . The complexity of this spectrum relative to that of a bulk sample reveals that the modes are significantly perturbed relative to that normally expected for methine, methylene, and methyl groups. Further evidence of the perturbation of the $\nu_{\text{C-H}}$ spectra is obtained by analysis of the features seen in the figure below 2800 cm^{-1} . The broad, poorly defined feature spanning between ~ 2350 and 2700 cm^{-1} arises from mode softening due to the direct metal···H–C contacts. The substantial line width seen here has been observed for other unsubstituted cycloalkane adsorbates,^{31,32} although the effect seen for this adsorbate appears to be exceptionally large. The spectrum of the multilayer, after subtraction of the contribution due to the surface-contacting layer, is somewhat less complex. The difference spectrum, which essentially removes contributions due to the monolayer, is dominated by modes appearing at frequencies typical for unperturbed CH_3 and CH_2 groups; the most important features occur at 2849, 2917, and 2951 cm^{-1} , values corresponding to the CH_2 symmetric, CH_2 antisymmetric, and CH_3 antisymmetric stretching modes, respectively. The significant dichroism evident in these spectra is consistent with a preferred in-plane orientation of the ring relative to the surface (see below).

The mode softening evidenced in the monolayer spectrum shown in Figure 1 is exceptional in terms of the size of the frequency shift. While substantial effects have been described in the literature for cycloalkanes adsorbed on a variety of clean metal surfaces (especially cyclohexane),^{26–29} the data reported

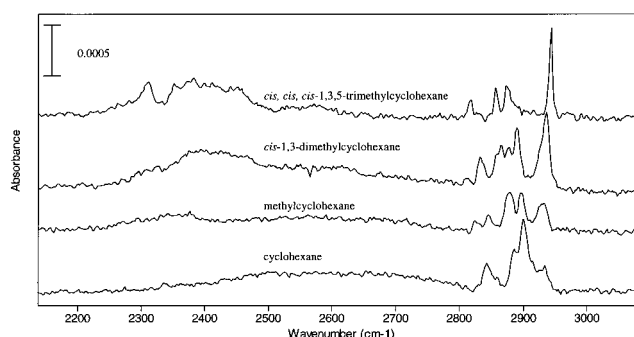


Figure 2. RAIR spectra of various cyclohexanes showing the dramatic changes seen in vibrational modes in the C–H stretching region with changes in the molecular structure of the adsorbate.

here suggest a heretofore unappreciated sensitivity to changes in the degree of methyl substitution for cyclohexanes adsorbed on Pt(111). Figure 2 shows the dramatic changes that are seen in the vibrational spectra in the C–H stretching region as a function of the number of methyl substituents on the cyclohexane ring. The spectrum of cyclohexane follows descriptions given in the literature, with prominent features seen at 2841, 2883, and 2900 cm^{-1} and a broad feature at low frequency (2400–2800 cm^{-1}) resulting from the adsorbate interactions occurring with the surface. This latter softened mode is broad and difficult to distinguish from a RAIRS baseline artifact. The spectrum of methyl cyclohexane shows a qualitatively similar pattern of bands; in the normal $\nu_{\text{C-H}}$ region, bands are seen at 2825, 2845, 2879, 2897, and 2931 cm^{-1} . In this case, however, an even broader envelope of softened modes is seen owing to metal interactions with the C–H bonds (spanning here from ~ 2250 to 2800 cm^{-1}). This pronounced and intensifying pattern of perturbations of the $\nu_{\text{C-H}}$ modes continues for the other methyl-substituted cyclohexanes examined here. The monolayer spectrum for *cis*-1,3-dimethylcyclohexane (as noted above) shows, in addition to modes in the normal C–H stretching region, an exceptionally intense and broad feature (~ 2300 –2480 cm^{-1}) due to the direct metal···H–C contacts. The RAIR spectrum of *cis,cis,cis*-1,3,5-trimethylcyclohexane, which completes the series studied, proved to be remarkable. Distinct features in the normal C–H stretching region appear at 2816, 2856, 2874, and 2943 cm^{-1} . These bands culminate a trend seen across the series, one in which the line widths of the bands seen above 2800 cm^{-1} narrow progressively as the degree of substitution of the ring increases. Several intense and broad features at 2309 cm^{-1} and a broad feature spanning from 2352 to 2461 cm^{-1} are seen in the region associated with C–H motions perturbed by metal contacts.

The pattern of the mode softening seen in the data presented in Figure 2 was unexpected. The factors that contribute to the magnitude of the effects seen, and their structural sensitivities, are not completely understood. On the basis of past work, we believe the line width of the softened-mode envelope reports sensitively on the adsorbate dynamics and the structural homogeneity of the metal···H–C contacts in the physisorbed layer.²⁵ One expects, then, that the degree of methyl substitution should sensitively impact both of these latter factors. A simple model, discussed for the specific case of *cis,cis,cis*-1,3,5-trimethylcyclohexane, illustrates one possible aspect of the line-broadening mechanism.

Methyl substitution grossly perturbs the conformational dynamics of a cyclohexyl ring;³³ the 3-fold substitution in *cis,cis,cis*-1,3,5-trimethylcyclohexane, owing to the increased burden of steric repulsion, is sufficient to yield an essentially locked

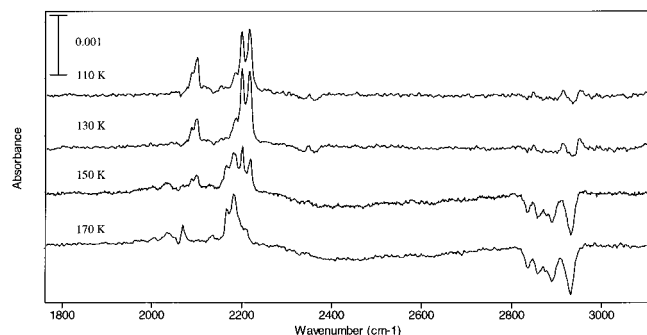
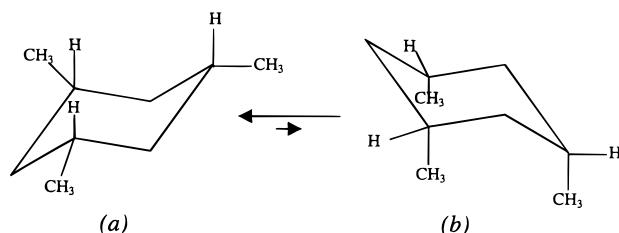


Figure 3. Temperature-dependent RAIR difference spectra of *n*-octane- d_{18} adsorbed on a monolayer of *cis*-1,3-dimethylcyclohexane on Pt(111). The coverage of *n*-octane- d_{18} was $\theta \approx 2.5\theta_s$.

conformation for the free molecule as illustrated in the structural scheme below.



It seems reasonable that this molecule would bind to Pt(111) in conformation a. We believe that this disklike projection can assemble in a very dense (almost gearlike) layer. Although we have not independently confirmed that this organizational state is present using diffraction methods, we feel it best accounts for the trends seen in the vibrational spectroscopy, namely, the magnitude and character of the mode softening and the narrow line widths of the bands appearing in the C–H stretching region above 2800 cm^{-1} . We must emphasize here, however, that this bound state (if correct) must lead to other as yet unaccounted for perturbations of the vibrational modes associated with nonmetal-contacting C–H segments. Given the simplifications that should result from the dipole selection rule,^{34,35} the latter simply appear to be too large in number and at highly atypical frequencies for it to be otherwise. To get a better understanding of these spectra, we believe it would be extremely useful to measure spectra at much lower temperatures than is possible with our current apparatus so that the effects of the low-frequency modes and perhaps thermal disorder could be more directly explored.^{36,37}

We turn now to a consideration of the transport dynamics of thin films formed by these adsorbates on Pt. We explore this by both RAIR and TPD spectroscopies and present the results of each in turn.

***cis*-1,3-Dimethylcyclohexane with *n*-Octane- d_{18} .** Figure 3 presents a set of RAIR difference spectra that monitor the evolution of a mixed multilayer, formed by the deposition of *n*-octane- d_{18} , ($\theta \approx 2.5\theta_s$) onto a Pt(111) surface previously covered with a monolayer of *cis*-1,3-dimethylcyclohexane, as a function of temperature. At 110 K, peaks at 2199 and 2218 cm^{-1} are observed, which we assign to the expected antisymmetric methylene and methyl C–D stretches of *n*- C_8D_{18} molecules present in the multilayer. Small negative features are also seen at 2932 cm^{-1} , indicative of a slight perturbation (loss of intensity) of the C–H modes of the surface-contacting molecules. After the surface is warmed briefly to 130 K, we see few changes. Flash-annealing to 150 K, however, produces large changes in the spectra. In the C–D region, the original

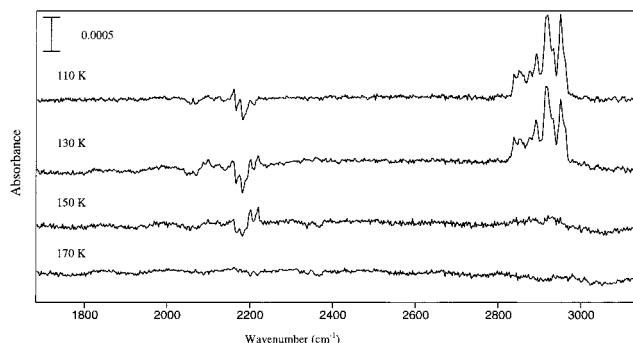


Figure 4. Temperature-dependent RAIR difference spectra of *cis*-1,3-dimethylcyclohexane adsorbed on a monolayer of *n*-octane- d_{18} on Pt(111). The coverage of *cis*-1,3-dimethylcyclohexane was $\theta \approx 2\theta_s$.

bands all decrease in intensity and a new feature appears in the spectrum at 2186 cm^{-1} . This latter mode is characteristic of C–D segments in contact with the surface. In the C–H region, the spectra are dominated by negative intensity features at 2833, 2854, 2890, and 2930 cm^{-1} (with no $\nu_{\text{C-H}}$ modes appearing for multilayer species), thus indicating the loss of a significant fraction of the molecules that were initially in contact with the surface. Some C–D segments are retained in the multilayer, however. The appearance of the softened C–H modes in this spectrum as a negative intensity feature is clearly evident. As we show below, the multilayer species begin to desorb at temperatures near 150 K. Increasing the annealing temperature to 170 K results in a further exchange of *n*-octane- d_{18} molecules for a significant portion of the initially surface-contacting *cis*-1,3-dimethylcyclohexane adsorbate. As judged from an integration of the C–D absorption bands relative to that of an authentic monolayer, we estimate that about 40% of the *cis*-1,3-dimethylcyclohexane is displaced by the 2.5 monolayer equivalents of *n*-octane- d_{18} initially bound in the multilayer.

An examination of the same system deposited in the reverse order shows a strong preference for the retention of the linear molecule at the surface. Figure 4 shows the temperature dependence of the RAIR spectra obtained in this experiment. The data clearly show that a modest amount of interlayer mixing occurs at temperatures between 130 and 150 K. This mixing is largely reversible because, as the temperature is raised further to 170 K, a nearly featureless difference spectrum is obtained. Given that the difference spectrum shown here is calculated against a single-beam of an *n*-octane- d_{18} monolayer, the lack of holes in the C–D region and the absence of C–H bands of measurable intensity suggest a nearly complete retention of the linear chains in the monolayer.

Cyclooctane with *n*-Octane- d_{18} . We further investigated the nature of the interlayer exchange dynamics by examining a related mixed pairing of hydrocarbons with similar molecular weights (*n*-octane- d_{18} and cyclooctane). Reference spectra of cyclooctane are given in the Supporting Information. Figure 5 shows the temperature dependence of the RAIR spectra of *n*-octane- d_{18} adsorbed with an initial coverage of $\theta \approx 2\theta_s$ on a monolayer of cyclooctane at 110 K. The modes seen in the C–D region between 2100 and 2300 cm^{-1} at 110 K correspond mostly to *n*-octane- d_{18} molecules in a multilayer. The corresponding C–H stretching region (2800 – 3000 cm^{-1}) shows large difference bands, suggesting that the contacting overlayer of the *n*-alkane significantly perturbs the vibrational modes of the surface-bound cycloalkane. It is not clear whether these latter effects arise strictly from a solvation effect or from some degree of competitive binding of C–D groups to the surface (which might shift or displace C–H segments from positions occupied

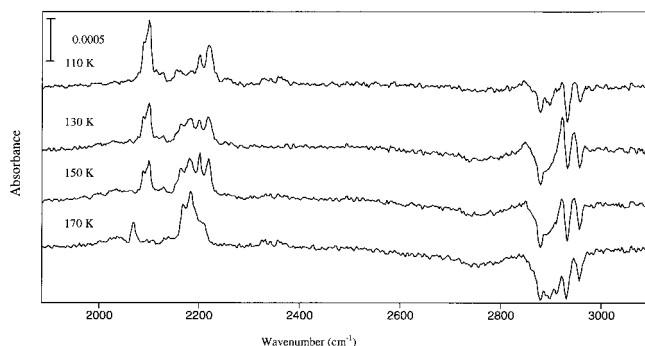


Figure 5. Temperature-dependent evolution of the RAIR difference spectra of *n*-octane-*d*₁₈ adsorbed on a monolayer of cyclooctane on Pt(111). The coverage of *n*-octane-*d*₁₈ was $\theta \approx 2\theta_s$.

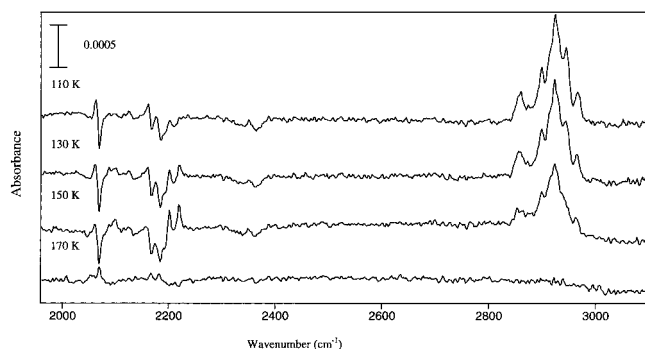


Figure 6. Temperature-dependent evolution of the RAIR difference spectra of cyclooctane adsorbed on a monolayer of *n*-octane-*d*₁₈ on Pt(111). The coverage of cyclooctane was $\theta \approx 3\theta_s$.

in the monolayer). After the surface is flash-annealed to 130 K, modes characteristic of C–D metal contacts are clearly visible at 2168 and 2183 cm^{-1} in the RAIR spectra. This interaction is accompanied by the removal of cyclooctane from the surface via displacive exchange (as suggested by the complex series of difference bands seen between 2881 and 2948 cm^{-1}). These changes become more pronounced with increasing annealing temperature, and, by 170 K, all molecules in the multilayer have desorbed, leaving behind a significant fraction of surface-bound *n*-octane-*d*₁₈. By using the integration method described earlier, we estimate that $\sim 95\%$ of the surface-bound cyclooctane is removed via displacive exchange with the two monolayer equivalents of *n*-octane-*d*₁₈ initially present in the multilayer. As argued before, these results suggest considerable mobility for the molecules bound in the assembly and, for comparable sized alkanes, a strong bias for the retention of the linear molecule; the branched cyclic adsorbate (*cis*-1,3-dimethylcyclohexane) appears to interact more strongly with the substrate than does cyclooctane, however. A quantitative analysis of these trends was obtained from temperature-programmed desorption data, a point we will return to later.

Figure 6 shows RAIR difference spectra for the same adsorbates as described immediately above, only here deposited in the reverse order. Specifically, three monolayer equivalents of cyclooctane ($\theta \approx 3\theta_s$) were adsorbed onto a monolayer of *n*-octane-*d*₁₈ at 110 K. The spectra suggest that little displacive exchange occurs at this temperature; a “solvation” effect on the magnitudes of the transition moments for the C–D stretching modes is evident, however. At higher flash-annealing temperatures, the complex difference bands change in ways that suggest that some of the *n*-octane-*d*₁₈ segments have been lifted from the surface (most notably the modes seen at 2200 and 2218 cm^{-1}). By 170 K, the multilayer desorbs and an essentially featureless baseline is obtained in the high-frequency region (as

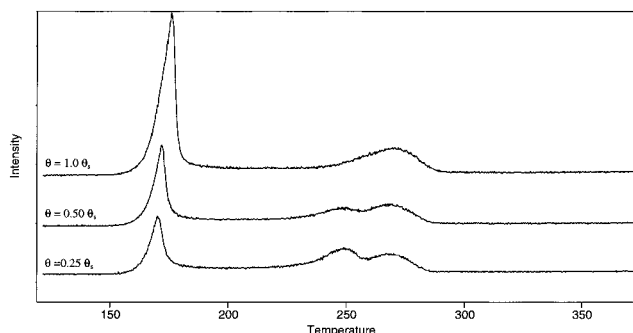


Figure 7. TPD data for varying coverages of *n*-octane-*d*₁₈ adsorbed on a Pt(111) single-crystal surface that had been precovered with a monolayer of cyclooctane. Desorption was followed at $m/e = 41$, an ion specific for the unlabeled adsorbate.

expected for an organization of the remaining molecules that is nearly identical to the reference, i.e., a monolayer of *n*-octane-*d*₁₈).

We turn now to a consideration of TPD data that more precisely quantifies the exchange processes occurring in the multilayer assemblies and provides estimates of the energetics associated with the various bound states of the adsorbate molecules.

Temperature-Programmed Desorption from Cyclooctane/*n*-Octane-*d*₁₈ Bilayers. Temperature-programmed desorption data for cyclooctane and *n*-octane-*d*₁₈ multilayer assemblies provide some additional insights into the displacive exchange processes occurring as a function of temperature. Figure 7 shows temperature-programmed desorption spectra for varying coverages of *n*-octane-*d*₁₈ adsorbed on a monolayer of cyclooctane measured for the cracking fragment at $m/e = 41$, an ion specific to the desorption of the latter adsorbate. If no displacements or reorganizations were occurring in this system, we should observe only one desorption feature at 250 K corresponding to the desorption of cyclooctane from the monolayer. In fact, though (for all the multilayer coverages examined), at least two peaks are seen. The spectra shown in Figure 7 correspond to *n*-octane-*d*₁₈ coverages in the multilayer of 1.00, 0.50, and $0.25\theta_s$. For coverages of both 0.50 and $0.25\theta_s$ of *n*-octane-*d*₁₈, there are in fact three peaks seen in the TPD data (at 170, 250, and 275 K). The feature at 170 K clearly corresponds to desorption from the multilayer; the features at 250 and 275 K correspond to desorption from the monolayer but obviously for states differing in the degree to which lateral interactions contribute to the surface binding energy of the *c*-C₈ adsorbate. Finally, at higher coverages in the overlayer, substantial fractions of the cyclooctane are exchanged and that which remains bound to the surface desorbs in a peak centered at 275 K. The reference spectra shown in Figure 8 demonstrate that the desorption of cyclooctane from a pure adlayer gives a peak maximum at 250 K for the monolayer state, while that for the higher boiling *n*-octane-*d*₁₈ occurs at 275 K. We find it remarkable that an appreciable quantity of the cyclooctane desorbing from a mixed adlayer behaves as though it were “entrapped” by the *n*-octane-*d*₁₈ molecules. This result clearly suggests that, at these coverages in a mixed monolayer, the molecules must remain mixed to a significant degree. We do not believe it likely, however, that the *n*-alkanes would penetrate the rings and pin the adsorbate as in analogy, for example, with a Velcro fastener. Rather, we believe it is likely that the perturbations originate from the complex kinetics associated with desorption from adsorbate domains bound by strong attractive lateral interactions (see below).

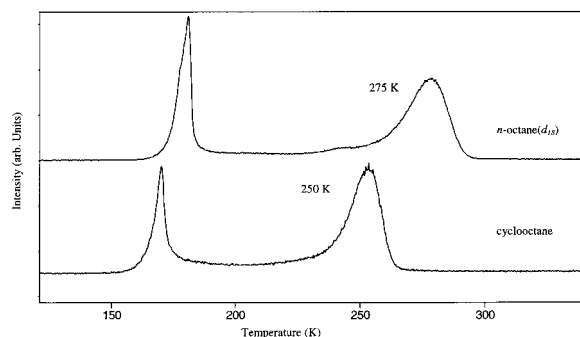


Figure 8. Comparative TPD spectra of a cyclooctane ($m/e = 41$) and n -octane- d_{18} ($m/e = 50$) multilayer on Pt(111).

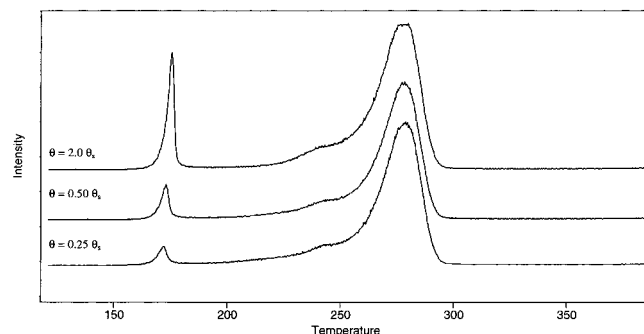


Figure 9. TPD data for varying coverages of adsorbed cyclooctane on a Pt(111) single-crystal surface that had been precovered with a monolayer of n -octane- d_{18} . Desorption was followed at $m/e = 50$, an ion specific for the deuterium-labeled adsorbate.

Figure 9 shows temperature-programmed desorption spectra for varying coverages of cyclooctane adsorbed onto n -octane- d_{18} with the ion followed ($m/e = 50$) corresponding only to desorption of the n -alkane. The coverages of cyclooctane used are $\theta = 1.00$, 0.50 , and $0.25\theta_s$. At a one-quarter monolayer coverage of cyclooctane, features are seen at 175 and 275 K corresponding to the desorption of n -octane- d_{18} molecules present as both multilayer and monolayer bound species, respectively. As the initial coverages in the multilayer increase, larger fractions of the n -alkane are exchanged. The fraction exchanged, however, is always less than that obtained in the inverse order for comparable coverages. The trend thus confirms the earlier finding of a strong tendency in this system to retain the n -alkane over the cycloalkane.

This trend can be more rigorously quantified by integration and self-normalization of the coverage-dependent TPD traces, as described in an earlier report.¹⁵ These data are shown in Figure 10. At all multilayer coverages, the amount of cyclooctane displaced (by n -octane- d_{18}) is greater than the amount of n -octane- d_{18} displaced (in an inverse ordering of the adsorbate layers). For coverages up to four layers of cyclooctane on n -octane- d_{18} , only about 20% of the surface-bound n -octane- d_{18} is displaced, while at four layers of n -octane- d_{18} on cyclooctane, approximately 80% of surface-bound cyclooctane is displaced. These findings support the RAIRS data and demonstrate a fundamental structural correlation in which linear molecules easily displace cyclic molecules of comparable size. A less extensive survey (data not shown) suggests that a similar, though less dramatic, structure/rate/property correlation exists for the n -octane- d_{18} and *cis*-1,3-dimethylcyclohexane system as well.

Concluding Remarks

Taken together, the data presented above shed light on a number of interesting behaviors exhibited by thin hydrocarbon

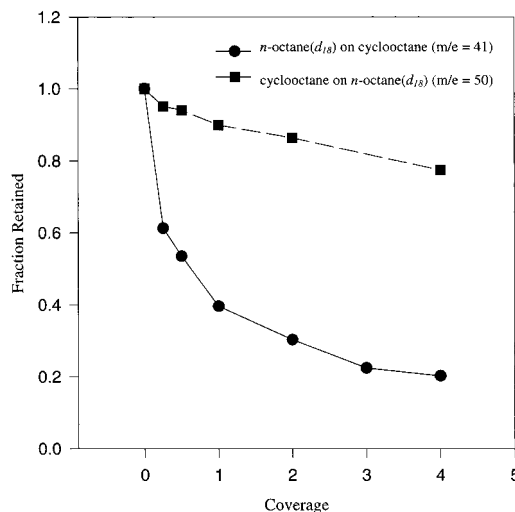


Figure 10. Displacive exchange of initially bound n -octane- d_{18} by various coverages of cyclooctane compared to the displacive exchange of initially bound cyclooctane by various coverages of n -octane- d_{18} on Pt(111).

assemblies and point out a number of poorly appreciated facts regarding the nature of their binding interactions on metal surfaces.

First, there does not appear to exist a simple (or more likely, any) correlation between the mode softening seen for a hydrocarbon adsorbate and the strength of its binding. We find, for example, substantial effects in the vibrational spectra of the cycloalkanes and yet see no strong correlation between this fact and either the TPD data or the tendency for retaining this adsorbate relative to a linear alkane at the surface in a mixed assembly. For the most part, the strength of the binding appears to directly follow differences in bulk thermodynamic properties (such as the boiling points). The effects of lateral interactions (see below) can complicate this correspondence for mixed adsorbate layers.

Second, we see (as reported by us before)¹⁵ that hydrocarbon multilayer assemblies on Pt(111) are extremely dynamic even while maintaining a high degree of overall orientational and organizational structure. Thus, even at temperatures well below the threshold for multilayer desorption, substantial exchange between the multilayer and the more strongly bound surface layer is seen.

Third, as is perhaps most strongly inferred from the unusual kinetics seen for the mixed n -octane- d_{18} /cyclooctane system, strong attractive lateral interactions make extremely important contributions to the thermodynamics and desorption kinetics of these phases. We believe this latter issue requires careful consideration in order to develop a clearer understanding of the phase behaviors seen in this prototypical class of organic thin-film material (or whenever the thermodynamics involved in the formation of an assembly are analyzed via a kinetic method such as TPD). Neglecting the effects of these interactions in a model could lead to mistaken interpretations of the structure/rate/property correlations that are important to the surface binding. For example, the abnormal surface binding energies that a first-order rate analysis would predict for cyclooctane bound in a mixed monolayer with n -octane (two states differing in binding energy by 1.8 kcal/mol)³⁸ are extremely hard to rationalize. We believe that the kinetics cannot be addressed in a physically plausible way without invoking phase effects (i.e., domains) that result from lateral interactions occurring within a mixed adsorbate overlayer. We will discuss this issue in more quantitative terms in a subsequent report.

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Supporting Information Available: RAIR spectra of cyclooctane on Pt(111). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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