Melting of Rodlike Molecules on Pt(111). Infrared Spectroscopic Studies of Isotopically Labeled \( n \)-Alkanes

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The melting of monolayers of isotopically labeled \( n \)-alkanes on Pt(111) surfaces has been followed by reflection-absorption infrared (RAIR) spectroscopy, and the results are compared with those of an earlier study of the unlabeled molecules (J. Phys. Chem. 1995, 99, 15629–15278). Temperature-dependent studies show that monolayers of the \( n \)-octane isotopolog, CD\(_3\)(CH\(_2\))\(_3\)CD\(_3\), melt on Pt(111) from a two-dimensionally ordered phase to one having one-dimensional order ("hexatic") near 220 K, a temperature essentially identical to that seen for unlabeled \( n \)-octane. The RAIR spectra of the labeled molecules generally confirm (but in one case clarify an overly simplistic interpretation of) the assignments of the bands made in the earlier study. Specifically, the assignment of a low-frequency "softened" mode near 2760 cm\(^{-1}\) to a \( \nu_{\text{CH}} \) stretch for proximal (i.e., surface-contacting) methylene C–H bonds has been verified. A feature near 2900 cm\(^{-1}\) had previously been assigned to a distal methylene C–H stretch, and the line width of this band was thought to increase as a result of the 2D \( \rightarrow \) 1D melting transition. The present study shows that this latter proposal is not entirely correct: the 2900 cm\(^{-1}\) feature actually consists of two bands separated by 5–15 cm\(^{-1}\) (for adsorbed \( n \)-octane) due to a Fermi resonance between a distal methylene C–H stretch and the first overtone of a methyl C–H bending mode. Owing to the small frequency difference between the split components of the Fermi resonance, these two bands partially overlap, and thus the appearance of the combined feature is largely determined by small changes in the relative frequencies of the methyl \( \delta_{\text{CH}} \) overtone and the methylene \( \nu_{\text{CH}} \) fundamental. The studies of the labeled \( n \)-alkanes confirm, however, that melting to the 1D phase is accompanied by distinct changes in the frequency of the low-frequency (softened) \( \nu_{\text{CH}} \) band near 2760 cm\(^{-1}\). More generally, these results establish unambiguously that the normal modes of an adsorbed \( n \)-alkane are very different from the normal modes of the free molecule because the low frequencies of the proximal C–H oscillators cause them to be decoupled from the distal C–H oscillators. An analysis of the temperature dependence of the softened \( \nu_{\text{CH}} \) mode using a critical temperature scaling model shows a correlation which can be rationalized in the context of the amplitude of the frustrated translational mode (the true low-frequency soft mode) that drives the (2D \( \rightarrow \) 1D) order–order transition in this system.

Introduction

There continues to be considerable interest in the chemical physics of phase transitions occurring in two dimensions.\(^1\) We recently described vibrational spectroscopic studies which elucidate the microscopic mechanisms via which monolayers of \( n \)-hexane, \( n \)-octane, and \( n \)-decane melt on Pt(111).\(^2\) At low temperatures, these \( n \)-alkanes form ordered overlayer systems in which the planes of the (all-trans) carbon backbones are parallel to the surface. As the temperature is raised the ordered overlayer melts, but interestingly the melting occurs in two stages: the 2D (two-dimensionally) ordered phase present at low-temperature melts first to a 1D (one-dimensionally) ordered phase and then (close to the desorption temperature of the adsorbate) to a disordered phase at higher temperatures. The transition temperature increases as the chain length of the \( n \)-alkane increases: the 2D \( \rightarrow \) 1D transition temperatures are approximately 187, 212, and 225 K for \( n \)-hexane, \( n \)-octane, and \( n \)-decane, respectively, while the corresponding 1D \( \rightarrow \) disordered phase transition temperatures are approximately 210, 240, and 270 K. Our spectroscopic studies, which suggested that the melting transitions are continuous, strongly support the conclusions of Firment and Somorjai who, in a pioneering study, first investigated the phase dynamics of \( n \)-alkane overlayers on Pt(111) by means of low-energy electron diffraction.\(^3\) The ideas developed in the experimental work have been supported more recently by the results of molecular-dynamics simulations of both melting processes (for butane) and diffusion of \( n \)-alkanes on Pt(111).\(^4\)–\(^6\) The complex nature of the phase transitions seen in these simulations is consistent with theoretical predictions (but do not compel) that the 2D \( \rightarrow \) 1D order–order transition need not be a single discontinuous transition, but, rather, can occur by means of an intermediate phase (sometimes referred to as a "hexatic" phase) whose properties are intermediate between those of the ordered solid and the disordered liquid.\(^7\)–\(^10\) These simulations also demonstrate that motional dynamics of these assemblies are also quite complex and sensitive to the chain length of the adsorbate.

On the basis of insights gained from spectroscopic studies, we have suggested that the loss of order at higher temperatures is correlated with the formation of gauche kinks defects in an otherwise predominantly all-trans chain. As have others, we suggested that these gauche kinks create open regions on the surface (essentially, a dislocation generating process known as footprint reduction\(^11\)\(^\text{a}^12\)) and that these open regions allow the
phase transitions to occur. The molecular-dynamics simulations further suggest that the onset of melting is further correlated with some degree of molecular motion perpendicular to the surface (i.e., an out-of-plane tilting of molecules).6

In our previous publication, we showed that the C–H stretches of n-alkanes adsorbed on Pt(111) at low temperatures can be divided into two sets: one set in the normal frequency range (2850–3000 cm$^{-1}$) and the other at unusually low frequencies (2600–2850 cm$^{-1}$).2 The bands above 2850 cm$^{-1}$ arise from the C–H bonds pointing away from (distal to) the surface, while the features below 2850 cm$^{-1}$ arise from C–H bonds pointing toward (proximal to) the surface. This arrangement is shown schematically below for the methylene and methyl segments in a prototypical chain.

The most intense of the low-frequency vibrational features, which are usually referred to as "softened" modes, appears at $\sim$2760 cm$^{-1}$. The $\sim$150 cm$^{-1}$ shift to lower frequency is the result of direct C–H···M interactions between platinum atoms and the proximal C–H bonds. An important conclusion of our earlier study was that the low frequencies of the proximal C–H oscillators causes them to be decoupled from the distal C–H oscillators that project away from the surface. For this reason, the normal modes of an adsorbed n-alkane are very different from those of the free molecule.

Interestingly, in the 2D ordered phase, the softened modes for these adsorbed n-alkanes are unusually sharp: the full-widths at half-maximum are less than 50 cm$^{-1}$ versus the nearly 150 cm$^{-1}$ line widths typically seen for adsorbates such as saturated cyclic hydrocarbons.13–24 In our previous study, we concluded that the line widths of softened modes are largely determined by the degree of site heterogeneity, i.e., the number of different local surface environments sampled by the proximal C–H bonds owing to the translational, rotational, and conformational freedom of the adsorbate. The relatively well-defined features and narrow line widths of the softened modes seen for n-hexane, n-octane, and n-decane on Pt(111) at low temperatures are consequences of three factors. First, these n-alkanes form ordered monolayers on the surface as indicated by LEED experiments.25 Second, molecules in the ordered monolayer are densely packed and have essentially no degrees of freedom. Third, the distance between methylene groups is nearly commensurate with the Pt–Pt distance on the Pt(111) surface. These three factors dictate that, in an all-trans conformational state, the proximal C–H bonds of the Pt-bound n-alkanes probe nearly identical surface sites.26

For n-alkanes on Pt(111), we found that the frequency of the softened mode at $\sim$2760 cm$^{-1}$ and the line width of the band at $\sim$2900 cm$^{-1}$ (assigned previously to the distal C–H stretches of the methylene groups) were especially sensitive to changes in the order of the adsorbate layer. The change in the appearance of the softened mode upon melting is understandable: the loss of translational order associated with the 2D $\rightarrow$ 1D phase transition means that the n-alkane molecules (and their proximal C–H bonds in particular) can sample a larger set of local environments. This increase in site heterogeneity for the proximal C–H bonds causes pronounced changes in the softened mode to which they give rise. The change in the band at 2900 cm$^{-1}$ upon melting was unexpected, however, since a feature assigned to motions of distal C–H bonds should not be particularly sensitive to changes in the order of the n-alkane overlayer.

In order gain additional insight into the nature of these two-dimensional melting phenomena, and to test the assignments made for the RAIR bands of adsorbed n-alkanes, we compared the variable-temperature RAIR spectra of adsorbed n-alkanes with those of selectively deuterated isotopologs. Among the labeled molecules we have investigated are CH$_3$(CH$_2$)$_2$CH$_2$, CD$_2$HCD$_2$(CH$_2$)$_2$CD$_2$H, CD$_3$(CH$_2$)$_2$CD$_2$H, and n-C$_6$D$_{18}$. Apart from the insights they afford into the melting of rodlike molecules on metal surfaces, these isotopically labeled species have made it possible to prove which modes are due to methyl versus methylene groups, and also to establish whether there are differences in the vibrational modes of chain-end vs interior methylene groups. We show, for example, that the previous assignment of the 2900 cm$^{-1}$ band to a distal C–H methylene stretch was only partially correct. More importantly, the current data allows us to construct a scaling analysis of the temperature dependence of the softened ν$_{CH}$ bond frequencies. This analysis supports the conclusion that the 2D $\rightarrow$ 1D order–order process is not a discontinuous transition.

**Experimental Section**

The ultrahigh vacuum (UHV) chamber used in this work has been described previously;27 only a summary will be given here. The reflection–absorption infrared (RAIR) spectroscopic studies were performed in a stainless steel chamber equipped with turbomolecular and titanium sublimation pumps, an ion sputtering gun, a mass spectrometer for collecting temperature-programmed reaction spectra (TPRS), and an Auger electron spectrometer (AES); the base pressure was $\sim$3.0×$10^{-10}$ Torr. A Digilab FTS 60A spectrometer with a broad-band, liquid-nitrogen-cooled, MCT detector was used to collect the RAIR spectra. Typically, 1024 or 4096 scans were collected at 4 cm$^{-1}$ resolution for each sample, giving acquisition times of approximately 7 or 28 min, respectively. The Pt(111) crystal was purchased from Cornell Laboratories, oriented to within 0.5°, and polished to a fine mirror finish by metallographic techniques. The crystal was cleaned by heating it in the presence of $1 \times 10^{-6}$ Torr of O$_2$ for 3 min followed by annealing it at 1000 K for 2 min. For properly cleaned crystals no carbon or oxygen was detectable on the crystal surface by AES.

Unlabeled n-alkanes (propane through decane) and n-C$_6$D$_{18}$ were purchased from Aldrich (>99% pure) and were degassed before introduction into the chamber by a freeze/pump/thaw technique. The isotopically labeled alkanes, CD$_2$(CH$_3$)$_2$CD$_2$, CH$_3$CH$_2$(CD$_2$)$_2$CD$_2$CH$_3$, and CD$_2$HCD$_2$(CH$_2$)$_2$CD$_2$H, were prepared according to literature methods,26–30 and their purities were checked by GC, IR, and NMR methods. The alkanes were introduced into the chamber through an effusive doser positioned $\sim$5 cm from the crystal face. Coverages are given relative to a saturation coverage (1 monolayer) of the adsorbate ($\theta_{sa}$).

The RAIR spectra of the saturated monolayers were obtained by dosing the specified n-alkane onto a platinum(111) crystal kept at a temperature above the multilayer desorption temperature but below the monolayer desorption threshold. The formation of a saturated monolayer was confirmed when the intensity of the RAIR peaks no longer increased with the exposure. To obtain a RAIR spectrum of C$_6$D$_{18}$ free of CO bands, the surface was saturated with a monolayer of n-hexane at $\sim$200 K, cooled to $\sim$110 K, heated to $\sim$165 K while being exposed to C$_6$D$_{18}$, and finally cooled to 110 K. This process
results

General features of the RAIR spectra of adsorbed n-alkanes. In our previous paper,2 we described the reflection—absorption infrared (RAIR) spectra of n-hexane, n-octane, and n-decane adsorbed on Pt(111). Figure 1 gives the RAIR spectra of saturated monolayer coverages for a larger series of n-alkanes—from n-butane to n-decane—adsorbed on Pt(111) at 110 K. Mode assignments are in shown Table 1. At this temperature, all of these n-alkanes form two-dimensionally ordered overlayers in which the plane of the carbon backbone is parallel with the surface.3 The bond-orientational ordering, combined with the surface selection rules for RAIR spectroscopy on metal surfaces,32–35 considerably aids in assigning the vibrational bands.

The trends seen in the RAIR spectra as the chain length of the n-alkane increases are particularly revealing. Two of the features, those at ~2900 and 2760 cm−1, become relatively more intense and thus must be assigned to C–H stretching motions of the methylene groups. The presence of two widely separated features assignable to methylene stretching modes provides clear evidence that the normal modes of a surface-bound alkane are very different from those of the corresponding free molecule. When viewed in qualitative terms, the data suggest (as noted in our earlier paper) that the 2900 cm−1 feature arises from distal C–H methylene bonds (Hd in the diagram) that are pointing away from the surface, while the 2760 cm−1 feature (the “softened” mode) arises from proximal C–H methylene bonds (Hb) that are perturbed by interactions with the surface.2 The bands at ~2930 and 2945 cm−1 arise from in-phase (Hb + Hc in the diagram) and out-of-phase (Hb − Hc) stretching motions of the two distal C–H methyl bonds, while the band near 2820 cm−1 is tentatively ascribed to the proximal C–H methyl stretch (Hd).

The feature at ~2900 cm−1 actually contains two overlapping components (Figure 2), a fact not explained in our earlier publication. The frequency difference between these two components decreases from 15 cm−1 for n-butane to ~6 cm−1 for n-decane. One possibility is that one of these two components is due to methylene groups that are close to the chain termini and the other is due to “internal” methylene groups. Since the lower frequency component appears to become relatively more intense as the chains become longer, this component might be assignable to the internal methylene groups. This possibility can be ruled out, however, by the observation that n-butane shows two components in this region, despite the fact that all of the methylene groups are identical in terms of their distance from the chain termini. The actual origin of the two components is discussed below.

The RAIR spectrum of a submonolayer of n-octane on Pt(111) at 110 K is, in qualitative terms, relatively insensitive to coverage (Figure 3). Even at low coverages (θ = 0.22θsat), the spectrum closely resembles that of a full monolayer (other than for the absolute band intensities). This observation suggests that n-alkanes form islands at low coverages, which in turn suggests that adsorbate–adsorbate interactions play an important role in the organization of the overlayer. At higher coverages (shown here for θi = 1.5θsat), significant changes are seen in the RAIR spectra due to the growth of a second layer or multilayer.31 Adsorbates in the second layer differ from molecules in the first layer in two ways. First, their vibrational spectra show no perturbations due to the surface, so that their normal modes and vibrational frequencies resemble those of the unbound molecule.36,37 Second, their carbon backbones do not appear to lie exclusively parallel to the surface. The RAIR spectra of the assemblies contain new features at 2855, 2880, and 2960 cm−1. Formation of the second layer also is signaled
by broadening of the peak at \( \sim 2930 \text{ cm}^{-1} \). These new bands can be assigned in a straightforward manner based on the characteristic frequencies observed for \( n \)-alkane molecules in the gas or liquid phase: \(^{36,37} \) (the bands at \( \sim 2855 \) and \( 2930 \text{ cm}^{-1} \) are the symmetric and antisymmetric stretches, respectively, of the methylene groups while the bands at \( \sim 2880 \) and \( 2960 \text{ cm}^{-1} \) are the symmetric and antisymmetric stretches of the methyl groups. These new bands increase in intensity as the coverage is increased further (data not shown).

**RAIR Spectra of Isotopically Labeled \( n \)-Hexanes.** The assignments of the vibrational bands given previously for unlabeled \( n \)-alkanes on Pt(111) surfaces \(^2 \) have been tested by investigating the RAIR spectra of the isotopically labeled \( n \)-hexanes \( \text{CH}_3(\text{CH}_2)_n\text{CH}_3 \) and \( \text{CD}_2\text{HCD}_2(\text{CH}_2)_n\text{CD}_2\text{HCD}_2 \) (see Table 2). These two molecules enable us to distinguish methyl modes from methylene modes and also allow us to distinguish bands due to methylene groups near the chain ends from those near the middle of the chain. The latter distinction is relevant to the assignment of the two components contributing to the feature centered near \( 2900 \text{ cm}^{-1} \).

Monolayers of unlabeled \( n \)-hexane and the two labeled \( n \)-hexane isotopologs \( \text{CD}_2\text{HCD}_2(\text{CH}_2)_n\text{CD}_2\text{HCD}_2 \) differ from those of \( n \)-alkanes near \( 2900 \text{ cm}^{-1} \) in one other important respect: the \( \text{C}--\text{H} \) distal methyl stretching bands appear as a single sharp band at \( 2916 \text{ cm}^{-1} \) rather than as two bands at \( \sim 2926 \) and \( 2945 \text{ cm}^{-1} \). In unlabeled \( n \)-hexane, the two bands arise from the in-phase and out-of-phase combinations of the two \( \text{C}--\text{H} \) distal bonds. In \( \text{CD}_2\text{HCD}_2(\text{CH}_2)_n\text{CD}_2\text{HCD}_2 \) there is only one \( \text{C}--\text{H} \) bond in each methyl group. If the hydrogen atom occupies site \( H_c \) in the diagram above, the transition moment for the \( \text{C}--\text{H} \) bond is less intense for the labeled molecule near the chain ends rather than the chain interior. Most notable is that the \( \text{C}--\text{H} \) distal methyl stretching bands appear as a single sharp band at \( 2889 \text{ cm}^{-1} \). The frequency of this band is about halfway between those of the two components seen for unlabeled \( n \)-hexane.

The RAIR spectrum of \( \text{CD}_2\text{HCD}_2(\text{CH}_2)_n\text{CD}_2\text{HCD}_2 \) differs from those of \( n \)-hexane isotopologs \( \text{CD}_2\text{HCD}_2(\text{CH}_2)_n\text{CD}_2\text{HCD}_2 \) and \( \text{CH}_3\text{CH}_2(\text{CD}_2)_n\text{CH}_3 \) in one other important respect: the \( \text{C}--\text{H} \) distal methyl stretching bands appear as a single sharp band at \( 2916 \text{ cm}^{-1} \) rather than as two bands at \( \sim 2926 \) and \( 2945 \text{ cm}^{-1} \). In unlabeled \( n \)-hexane, the two bands arise from the in-phase and out-of-phase combinations of the two \( \text{C}--\text{H} \) distal bonds. In \( \text{CD}_2\text{HCD}_2(\text{CH}_2)_n\text{CD}_2\text{HCD}_2 \) there is only one \( \text{C}--\text{H} \) bond in each methyl group. If the hydrogen atom occupies site \( H_c \) in the diagram above, the transition moment for the \( \text{C}--\text{H} \) bond is less intense for the labeled molecule near the chain ends rather than the chain interior. Most notable is that the \( \text{C}--\text{H} \) distal methyl stretching bands appear as a single sharp band at \( 2889 \text{ cm}^{-1} \). The frequency of this band is about halfway between those of the two components seen for unlabeled \( n \)-hexane.

The RAIR spectrum of \( \text{CD}_2\text{HCD}_2(\text{CH}_2)_n\text{CD}_2\text{HCD}_2 \) differs from those of \( n \)-hexane isotopologs \( \text{CD}_2\text{HCD}_2(\text{CH}_2)_n\text{CD}_2\text{HCD}_2 \) and \( \text{CH}_3\text{CH}_2(\text{CD}_2)_n\text{CH}_3 \) in one other important respect: the \( \text{C}--\text{H} \) distal methyl stretching bands appear as a single sharp band at \( 2916 \text{ cm}^{-1} \) rather than as two bands at \( \sim 2926 \) and \( 2945 \text{ cm}^{-1} \). In unlabeled \( n \)-hexane, the two bands arise from the in-phase and out-of-phase combinations of the two \( \text{C}--\text{H} \) distal bonds. In \( \text{CD}_2\text{HCD}_2(\text{CH}_2)_n\text{CD}_2\text{HCD}_2 \) there is only one \( \text{C}--\text{H} \) bond in each methyl group. If the hydrogen atom occupies site \( H_c \) in the diagram above, the transition moment for the \( \text{C}--\text{H} \) bond is less intense for the labeled molecule near the chain ends rather than the chain interior. Most notable is that the \( \text{C}--\text{H} \) distal methyl stretching bands appear as a single sharp band at \( 2889 \text{ cm}^{-1} \). The frequency of this band is about halfway between those of the two components seen for unlabeled \( n \)-hexane. The significance of this observation will be considered in the Discussion.

<table>
<thead>
<tr>
<th>( n )-alkane</th>
<th>( \nu(\text{C}--\text{H}_{\text{proximal}}) )</th>
<th>( \nu(\text{C}--\text{H}_{\text{distal}}) )</th>
<th>( \nu(\text{C}--\text{H}_{\text{distal}}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3(\text{CH}_2)_n\text{CH}_3 )</td>
<td>( 2666, 2752, 2817 )</td>
<td>( 2894 )</td>
<td>2903, 2928, 2947</td>
</tr>
<tr>
<td>( \text{CD}_2\text{HCD}_2(\text{CH}_2)_n\text{CD}_2\text{HCD}_2 )</td>
<td>( 2681, 2751, 2820 )</td>
<td>( 2889 )</td>
<td>2916</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CH}_2(\text{CD}_2)_n\text{CH}_3 )</td>
<td>( 2735, 2820 )</td>
<td>( 2897 )</td>
<td>2926, 2945</td>
</tr>
</tbody>
</table>

*Frequencies are given in cm\(^{-1}\).*
Figure 5. RAIR spectrum of a saturated monolayer of $n$-C$_{6}$D$_{18}$ on Pt(111) at 110 K.

Figure 6. RAIR spectra of saturated monolayers of (top) $n$-C$_{3}$H$_{8}$ and (bottom) CD$_{3}$(CH$_{2}$)$_{6}$CD$_{3}$ on Pt(111) at 110 K.

Finally, the RAIR spectrum of CD$_{3}$HCD$_{2}$(CH$_{2}$)$_{2}$CD$_{2}$CD$_{3}H$ exhibits a well-defined softened mode at $\sim$2760 cm$^{-1}$ due to the C–H$_{\text{proximal}}$ stretching motions of the interior methylene groups. The frequency of this band is very similar to that seen for unlabeled $n$-C$_{6}$H$_{14}$. In view of the lower frequency of the softened mode due to the chain-end methylene units, this observation suggests that the internal C–H$_{\text{proximal}}$ stretching motions are more intense than those of the chain-end C–H$_{\text{proximal}}$ methylene stretches, so that the former dominate the line shape in the spectrum of unlabeled $n$-C$_{6}$H$_{14}$.

**RAIR Spectra of Isotopically Labeled $n$-Octanes.** We have also investigated the RAIR spectra of two deuterated $n$-octanes: CD$_{3}$(CH$_{2}$)$_{6}$CD$_{3}$ and $n$-C$_{6}$D$_{18}$ (Figures 5 and 6, see Tables 3 and 4). Carbon–deuterium bonds have low oscillator strengths and thus are often difficult to detect with acceptable signal-to-noise (S/N) in a RAIR experiment (this is the case for the deuterated $n$-hexanes discussed above). We have been able, however, to detect with good sensitivity the bands due to C–D stretches in the RAIR spectrum of a monolayer of $n$-C$_{6}$D$_{18}$ on Pt(111). The C–D stretching bands lie between 1950 and 2250 cm$^{-1}$ (Figure 5) and can be correlated with C–H bands seen for the unlabeled molecule $n$-C$_{6}$H$_{14}$. Table 4 summarizes the $\nu_{\text{C–H}}$:$\nu_{\text{C–D}}$ ratios for the corresponding vibrational features in the RAIR spectra of $n$-C$_{6}$H$_{14}$ and $n$-C$_{6}$D$_{18}$ monolayers on Pt(111). The experimental ratios range from 1.33 to 1.37 and are very close to the theoretical value calculated from the reduced masses: $\omega_{\text{C–D}}/\omega_{\text{C–H}} = (m_{\text{C–D}}/m_{\text{C–H}})^{1/2} = 1.36$.

As for the C–H stretches of $n$-alkanes on metal surfaces, the C–D stretching features can be divided into two sets: one set (lying between 2100 and 2250 cm$^{-1}$) in the “normal” frequency range and a second set (lying between 1900 and 2100 cm$^{-1}$) consisting of “softened” $\nu_{\text{C–D}}$ modes at much lower frequencies. The latter features are direct evidence of surface C–D...M interactions. Softened modes at similar frequencies have also been observed for cyclohexane-d$_{12}$ adsorbed on transition metals. 19,22 Like $n$-C$_{6}$H$_{18}$, the labeled molecule $n$-C$_{6}$D$_{18}$ gives a softened mode that appears to have structure: a feature at 2020 cm$^{-1}$ is particularly prominent.

For the partially deuterated $n$-octane CD$_{3}$(CH$_{2}$)$_{6}$CD$_{3}$, the two peaks at 2929 and 2947 cm$^{-1}$ seen for $n$-C$_{6}$H$_{18}$ are completely absent, and this observation confirms that these bands are due to C–H$_{\text{distal}}$ stretching motions of the methyl groups (Figure 6). The 2820 cm$^{-1}$ band seen for $n$-C$_{6}$H$_{18}$ is also absent, and this finding confirms that this feature arises from C–H$_{\text{proximal}}$ stretching motions of the methyl groups. The split band (1441 and 1447 cm$^{-1}$) assigned to the C–H bends of the methyl group shifts to a single band at $\sim$1051 cm$^{-1}$ in the labeled molecule.

The vibrational features present in the RAIR spectrum of CD$_{3}$(CH$_{2}$)$_{6}$CD$_{3}$ above 2600 cm$^{-1}$ are those that arise from C–H stretches of the methylene groups. The C–H$_{\text{proximal}}$ stretching motions give rise to a softened mode at 2766 cm$^{-1}$ (a frequency identical to that of unlabeled $n$-C$_{6}$H$_{18}$), while the C–H$_{\text{distal}}$ stretching motions produce the intense band at 2905 cm$^{-1}$.

Whereas for $n$-C$_{6}$H$_{18}$ the latter band has two distinct components, for CD$_{3}$(CH$_{2}$)$_{6}$CD$_{3}$ only a single (albeit asymmetric) component is evident. This observation provides an additional clue to the origin of the splitting seen in $n$-C$_{6}$H$_{18}$ (see below).

Significant changes occur in the organization of a saturated monolayer of CD$_{3}$(CH$_{2}$)$_{6}$CD$_{3}$ as the temperature is raised (Figure 7). Particularly notable is that the softened mode centered at $\sim$2760 cm$^{-1}$ begins to broaden by 155 K and, above 200 K, begins to shift to higher frequency. For comparison, Figure 7 also includes the temperature-dependent RAIR spectra of a saturated monolayer of $n$-C$_{6}$H$_{18}$. The spectroscopic changes evidenced over this temperature range are reversible. We note, though, that the initial annealing cycle does tend to narrow the line widths of some bands seen in the low-temperature spectra.

Figure 8 (which is an expansion of Figure 7) illustrates how the vibrational feature near 2900 cm$^{-1}$ changes as a function of temperature for monolayers of $n$-C$_{6}$H$_{18}$ and CD$_{3}$(CH$_{2}$)$_{6}$CD$_{3}$. For both molecules, the line width of this feature increases as the temperature is raised, but the details differ, as is discussed in the next section.

**Discussion**

**Vibrational Mode Assignments for Monolayers of $n$-Alkanes on Pt(111).** The RAIR spectra of the isotopically labeled $n$-alkanes studied here largely confirm the mode assignments derived from our previous studies of the unlabeled molecules (Tables 1–3).3 The bands at $\sim$2930 and 2945 cm$^{-1}$ arise from in-phase and out-of-phase stretching motions of the two distal C–H bonds of the methyl groups, the band centered near 2900 cm$^{-1}$ is assigned to the C–H$_{\text{distal}}$ stretching motions of the methylene groups, and the softened modes at $\sim$2760 and 2820 cm$^{-1}$ arise from the C–H$_{\text{proximal}}$ stretching motions of the methylene and methyl groups, respectively. There is also a split band at $\sim$1445 cm$^{-1}$ (not shown in Figure 1) which is assigned to C–H bending motions of the methyl groups. Upon deu-
TABLE 3: Mode Assignments for \( n\text{-C}_8\text{H}_{18} \) and \( n\text{-C}_8\text{D}_{18} \) on Pt(111)°

<table>
<thead>
<tr>
<th>( n\text{-alkane} )</th>
<th>( CX, \delta (C\text{-X}) )</th>
<th>( \nu (C\text{-H}_{\text{proximal}}) )</th>
<th>( CH_x, \nu (C\text{-H}_{\text{distal}}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n\text{-C}<em>8\text{H}</em>{18} )</td>
<td>1441, 1447</td>
<td>2669, 2758, 2818</td>
<td>2896 (sh), 2903</td>
</tr>
<tr>
<td>( \text{CD}_3\text{(CH}_2\text{)}_6\text{CD}_3 )</td>
<td>1051</td>
<td>2697, 2766</td>
<td>2905</td>
</tr>
</tbody>
</table>

° Frequencies are given in cm\(^{-1}\).

TABLE 4: Isotopic Frequency Shifts Seen in the RAIR Spectra of Saturated Monolayers of \( n\text{-C}_8\text{D}_{18} \) and \( n\text{-C}_8\text{H}_{18} \) on Pt(111)°

<table>
<thead>
<tr>
<th>mode assignment</th>
<th>( n\text{-C}<em>8\text{D}</em>{18} ) freq. ratio</th>
<th>( n\text{-C}<em>8\text{H}</em>{18} ) freq. ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl distal out-of-phase</td>
<td>2208</td>
<td>2947</td>
</tr>
<tr>
<td>methyl distal in-phase</td>
<td>2181</td>
<td>2929</td>
</tr>
<tr>
<td>methylene distal stretch</td>
<td>2166</td>
<td>2900</td>
</tr>
<tr>
<td>methylene proximal stretch</td>
<td>2033</td>
<td>2758</td>
</tr>
<tr>
<td>methyl bend</td>
<td>1053</td>
<td>1445</td>
</tr>
</tbody>
</table>

° Frequencies are given in cm\(^{-1}\).

Figure 7. Variable-temperature RAIR spectra of saturated monolayers of (left) \( n\text{-C}_8\text{H}_{18} \) and (right) \( \text{CD}_3\text{(CH}_2\text{)}_6\text{CD}_3 \) on Pt(111) at 110 K. Because the desorption of the \( n\text{-octanes} \) is significant at 235 and 245 K, the spectra at these temperatures were collected in the presence of a background pressure of the appropriate \( n\text{-octane} \).

Figure 8. Expanded view of Figure 7 showing the 2875–2960 cm\(^{-1}\) region in more detail.

Insights into the origin of the two components that make up the band near 2900 cm\(^{-1}\) were gained by performing these isotopic labeling studies. Our initial hypothesis was that these two components were assignable to \( C\text{-H}_{\text{distal}} \) stretches from methylene segments lying at various distances from the chain termini. In fact, different frequencies for the \( C\text{-H} \) stretching vibrations of the interior and exterior methylene groups of gaseous alkanes have been observed by Snyder et al.\(^{38}\) This hypothesis in the current context can be ruled out, however, from the following observation: the RAIR spectra of unlabeled \( n\text{-butane} \) and the \( n\text{-hexane} \) isotopolog \( \text{CH}_3\text{H}_2\text{(CD}_2\text{)}_2\text{CH}_2\text{H}_3 \) both contain a two-component feature near 2900 cm\(^{-1}\) despite having only “chain-end” methylene units.

In contrast, the RAIR spectrum of the \( n\text{-hexane} \) isotopolog \( \text{CD}_3\text{HCD}_2\text{(CH}_2\text{)}_2\text{CD}_3 \), which is deuterated at the chain ends rather than the chain interior, contains a single band at 2889 cm\(^{-1}\). Deuteration of the methyl groups shifts three vibrational features to lower frequencies by the expected \( C\text{-H}:C\text{-D} \) ratio: the \( C\text{-H}_{\text{distal}} \) methyl stretching modes at 2929 and 2947 cm\(^{-1}\) and the \( C\text{-H} \) methyl bending mode at \( \sim 1445 \) cm\(^{-1}\). Interestingly, twice the frequency of the latter mode (1445 \( \times 2 \) = 2890 cm\(^{-1}\)) corresponds closely to the frequency observed for the \( C\text{-H}_{\text{distal}} \) methylene vibration for \( n\text{-C}_8\text{H}_{18} \) (\( \sim 2900 \) cm\(^{-1}\)). We therefore propose that the two components seen near 2900 cm\(^{-1}\) arise from a Fermi resonance between the first overtone of the \( C\text{-H} \) bend of the methyl groups and the fundamental of the \( C\text{-H}_{\text{distal}} \) stretch of the methylene groups. Because the frequency difference between the methyl bend overtone and the methylene stretch fundamental is rather small, significant intensity borrowing occurs.

This explanation is consistent with the disappearance of the second band upon deuteration of the methyl groups of octane \( (\text{CD}_3\text{(CH}_2\text{)}_6\text{CD}_3) \) and with our observation that the lower-frequency component becomes more intense relative to the high-frequency component as the chain lengthens. We note, though, that the length of the chain has no direct influence; the lower-frequency component becomes more intense because the frequency difference between the two components decreases as the chain becomes longer. Intensity borrowing by means of the Fermi resonance mechanism is most pronounced if the overtone and fundamental have identical frequencies.

Interestingly, while the frequency of the \( C\text{-H}_{\text{distal}} \) methylene stretch is essentially independent of the location of the methylene unit within the chain, the frequency of the softened mode due to the \( C\text{-H}_{\text{proximal}} \) methylene stretches is \( \sim 15 \) cm\(^{-1}\) lower for methylene units adjacent to the methyl groups than for methylene units in the chain interior. This finding suggests that the methylene units near the chain ends may have slightly stronger interactions with the surface than do the interior methylene units.

Spectroscopic Indicators of Monolayer Phase Transitions: Methylene \( C\text{-H}_{\text{proximal}} \) and \( C\text{-H}_{\text{distal}} \) Stretching Vibrations. As shown in our earlier publication and by Firment and Somorjai, monolayers of \( n\text{-hexane} \), \( n\text{-octane} \), and \( n\text{-decane} \) on a Pt(111) surface and undergo phase transitions characteristic of two-dimensional films. The existence of three phases has been established: a 2D ordered phase which is present at low temperatures, a 1D ordered phase at intermediate temperatures, and a disordered phase at higher temperatures (near the desorption threshold). We proposed in our earlier publication that the 2D → 1D transition is correlated with two changes seen in the infrared spectra: the softened mode at \( \sim 2760 \) cm\(^{-1}\) due to the \( C\text{-H}_{\text{proximal}} \) methylene stretches begins to move to higher frequency and the band at \( \sim 2900 \) cm\(^{-1}\) due to the methylene \( C\text{-H}_{\text{distal}} \) stretches begins to broaden.
The behavior of \( \text{CD}_3(\text{CH}_2)_n\text{CD}_3 \) monolayers as a function of temperature provides us with an opportunity to test these correlations. This molecule is particularly informative because the C–H stretching region only contains bands due to the methylene groups. We find that, for both \( n\text{-C}_8\text{H}_{18} \) and \( \text{CD}_3(\text{CH}_2)_3\text{CD}_3 \), the softened mode at \( \sim2760 \text{ cm}^{-1} \) (due to the methylene C–H \( \text{proximal bonds} \)) begins to shift to higher frequency near 200 K (Figure 9). This temperature is experimentally indistinguishable from that established by LEED for the 2D → 1D phase transition. This finding shows that the intermolecular interactions, as well as the adsorbate–surface interactions, are very similar for \( n\text{-C}_8\text{H}_{18} \) and \( \text{CD}_3(\text{CH}_2)_3\text{CD}_3 \). The results also lend support to the contention that the change in the frequency of the softened mode is a consequence of a change in the order of the monolayer. In the 2D ordered phase, the C–H \( \text{proximal oscillators} \) form the strongest possible interactions with surface sites. As the disorder of the monolayer increases (upon approaching or passing through the phase boundary), the C–H \( \text{proximal oscillators} \) will interact with a larger set of surface sites. For most of the new surface sites sampled, the geometries of the interactions will be less favorable, i.e., less able to perturb the frequency of the C–H stretch. This mechanism thus suggests that the softened modes will shift to higher frequencies as weaker C–H•••M interactions become more prevalent.

Our studies of deuterated \( n \)-alkanes, however, do not support our earlier suggestion that the 2D → 1D phase transition is also correlated with changes seen in the line width of the two-component feature centered near 2900 cm\(^{-1}\), at least not in the direct way described on the basis of the data then available. For \( n\text{-C}_8\text{H}_{18} \), the line width of the combined feature is relatively constant below 200 K, but above this temperature (which corresponds to the boundary of the 2D → 1D phase transition), the line width increases from \( \sim13 \) to \( \sim20 \text{ cm}^{-1} \) at 245 K (Figure 10). In contrast, the single feature near 2900 cm\(^{-1}\) seen for \( \text{CD}_3(\text{CH}_2)_3\text{CD}_3 \) broadens steadily throughout the 110–240 K temperature range; there is no break seen near 200 K in the line width versus temperature curve.

For unlabeled \( n \)-alkanes, we now know that the feature near 2900 cm\(^{-1}\) actually consists of (at least) two components as a result of a Fermi resonance. As a consequence, for unlabeled \( n \)-alkanes the line width of this feature depends on both the frequency difference between the two Fermi components and their individual line widths. The natural line widths of the individual components increase steadily with temperature throughout the 110–240 K temperature range. Below 200 K, however, the line width of the combined feature is determined by the frequency difference between the two components. It is not clear whether the break that occurs in the line width versus temperature curve near the 2D → 1D phase transition temperature is coincidental. However, we now feel that the C–H\( \text{distal methylene oscillators} \) are not sensitive indicators of the underlying order of the overlayer.

The thermodynamics of the structural phase transitions taking place in this system in principle can be investigated through the temperature dependence of an appropriate vibrational mode. This analysis requires us to establish in the context of this discussion a different definition for the term “soft mode,” one that has a long tradition in a different area of the literature. The basic Cochran–Anderson description of a soft-mode arises from the application of Landau’s thermodynamic stability conditions to a simple one-dimensional oscillator model of a structural phase transition. This treatment, while too simplistic to capture the quantitative details of a structural phase transition, does provide good qualitative insights into the temperature-dependent evolution of the structural properties of a system and the underlying dynamics which drive the transition. These issues are defined by the two related equations given below:

\[
\eta = \eta_0(T - T_0)^\beta \tag{1}
\]
\[
\omega = \omega_0(T - T_0)^\gamma \tag{2}
\]

Equation 1 defines the temperature-dependent evolution of the order-parameter and eq 2, the related temperature-dependent frequency of the underlying phonon (or more frequently referred to as the soft mode) driving the transition. It is now understood that structural phase transitions in which two ordered forms of a crystal are interconverted (such as the order-order phase transition of interest here) show a soft-mode whose frequency goes to zero as the transition temperature \( T_0 \) is approached in either direction. Such modes were first observed by Raman in studies of structural phase transitions occurring in quartz. It is now understood that this mode characterizes the symmetry changes occurring at \( T_0 \) and, more importantly, that only one normal mode of motion can be involved. The temperature scaling of either \( \omega \) or \( \eta \) is given by a critical exponent, \( \beta \), whose value is expected to vary between 0.50 and 0.33 depending on whether the transition is best described by mean-field or non-mean-field approximations. For real systems where the interactions are short ranged or the critical point is approached very closely, the latter is generally true, and thus values of \( \beta \approx 0.33 \) are expected.

The 2D→1D order→order transition of a \( n \)-alkane monolayer on Pt(111) is expected to exhibit lattice dynamics similar to

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**Figure 9.** Temperature dependence of the frequency of the softened mode at \( \sim2760 \text{ cm}^{-1} \) for \( n\text{-C}_8\text{H}_{18} \) (■) and \( \text{CD}_3(\text{CH}_2)_3\text{CD}_3 \) (∗).

**Figure 10.** Temperature dependence of the line width of the feature at \( \sim2900 \text{ cm}^{-1} \) for \( n\text{-C}_8\text{H}_{18} \) (■) and \( \text{CD}_3(\text{CH}_2)_3\text{CD}_3 \) (∗).
that embodied in eqs 1 and 2. It is clear, however, that the temperature-dependent mode softening seen in the C–H stretching region cannot correspond to the same soft mode underlying the phase transition. Figure 11 shows a plot according to eq 2 for the softened νc–H modes of n-octane and the isotopomer CD3(CH2)3CD3. The linear correlation of the frequencies with ln(T0 – T) are striking. The apparent values of the critical exponents, β, have no real physical meaning in this case, however, as the values of the high frequency modes plotted here cannot correspond to those of the fundamental soft mode (essentially a phonon) driving the 2D → 1D phase transition. By way of reference, Wöll et al. have characterized and assigned a frustrated translational mode for a closely related ordered layer on Cu(111); this mode occurs at 93 K. This mode is not directly related to an adsorbate 2D → 1D phase transition, however, as it is polarized along the surface normal direction. Simulations of the translational modes of butane overlayers on Pt(111) predicted a vibration at 77 cm⁻¹; stronger damping is observed at high coverage.

As noted above the mode softening seen in the C–H stretching region reflects the nature (and strength) of the C–H•⋅M contacts. We believe the fluctuations occurring near the phase boundary (related to the soft-mode) allow a temperature-dependent range of these interactions to be sampled (and thus expressed in the high-frequency spectra). One expects, as a result, that the high-frequency modes could exhibit an apparent temperature scaling similar to that seen for the low-frequency soft modes. We expect that temperature-dependent studies of the low-frequency spectra will be needed to establish whether non-mean-field transition behaviors are important in this system. By way of reference, similar behaviors have been reported for the low-frequency frustrated translations of CO adsorbed on various metal surfaces.

We close by noting a feature in the present data which remains poorly understood, namely, the weak band(s) near 2860 cm⁻¹. Modes in this region are clearly due to segments experiencing direct C–H•⋅M interactions. The data suggest that these bands (or band) are closely associated with the methylene segments of the chains. It is not clear, however, why such a multiplicity should exist for the softened modes of these segments. The isotopic studies yield no definitive insights into this aspect of the data since the intensities (and positions) seen for the 2680 cm⁻¹ feature show a complex and nonintuitive dependence on the isotopic substitution patterns of both the methylene and methyl groups. Owing to the low intensity of this feature, it is not clear how valuable a marker it is for the order present in the monolayer.

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References and Notes

It is interesting to note that cyclohexane, which forms an ordered and commensurate overlayer on Pt(111), shows an exceptionally broad softened mode. We believe this molecule may retain rotational degrees of freedom at 100 K that allow the proximal C–H bonds to sample different surface sites. This heterogeneity leads to a broad softened mode, which is actually a convolution of many overlapping components.