

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, CD₃(CH₂)₆CD₃, 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 ν_{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 → 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 δ_{CH} overtone and the methylene ν_{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) ν_{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 ν_{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 → 1D) order–order transition in this system.

Introduction

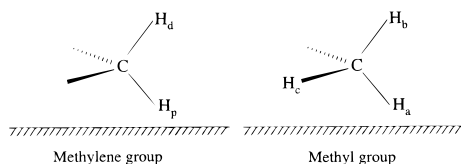
There continues to be considerable interest in the chemical physics of phase transitions occurring in two dimensions.¹ We recently described vibrational spectroscopic studies which elucidate the microscopic mechanisms via which monolayers of *n*-hexane, *n*-octane, and *n*-decane melt on Pt(111).² At low temperatures, these *n*-alkanes form ordered overlayers 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 temperatures increase as the chain length of the *n*-alkane increases: the 2D → 1D transition temperatures are approximately 187, 212, and 225 K for *n*-hexane, *n*-octane, and *n*-decane, respectively, while the corresponding 1D → 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 inves-

tigated 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 → 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^{11,12}) 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 onto 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 ~ 2760 cm⁻¹. The ~ 150 cm⁻¹ shift to lower frequency is the result of direct C–H \cdots 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 ~ 2760 cm⁻¹ and the line width of the band at ~ 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 CH₃CH₂(CD₂)₂-CH₂CH₃, CD₂HCD₂(CH₂)₂CD₂CD₂H, CD₃(CH₂)₆CD₃, and *n*-C₈D₁₈. 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 $\sim 3.0 \times 10^{-10}$ 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 1×10^{-6} Torr of O₂ 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*-C₈D₁₈ were purchased from Aldrich (> 99% pure) and were degassed before introduction into the chamber by a freeze/pump/thaw technique. The isotopically labeled alkanes, CD₃(CH₂)₆CD₃, CH₃CH₂(CD₂)₂CH₂CH₃, and CD₂HCD₂(CH₂)₂CD₂CD₂H, were prepared according to literature methods,^{28–30} and their purities were checked by GC, IR, and NMR methods. The alkanes were introduced into the chamber through an effusive doser positioned ~ 5 cm from the crystal face. Coverages are given relative to a saturation coverage (1 monolayer) of the adsorbate (θ_{sat}).

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 C₈D₁₈ free of CO bands, the surface was saturated with a monolayer of *n*-hexane at ~ 200 K, cooled to < 110 K, heated to ~ 165 K while being exposed to C₈D₁₈, and finally cooled to 110 K. This process

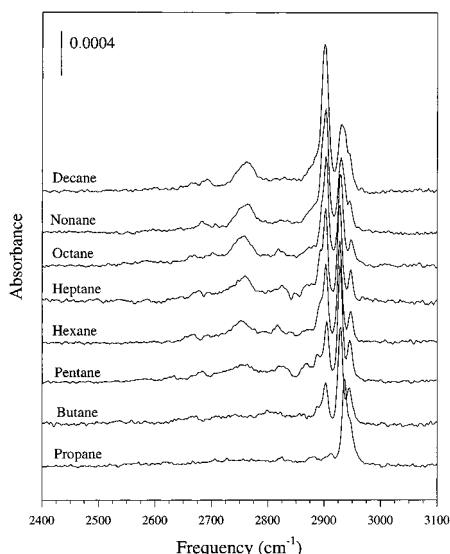


Figure 1. Reflection-absorption infrared spectra of saturated monolayers of *n*-propane through *n*-decane adsorbed on Pt(111). The specified *n*-alkane was dosed while the platinum crystal was at a temperature above the multilayer desorption threshold but below the monolayer desorption threshold of the adsorbate. The spectra were acquired at 110 K.

TABLE 1: Mode Assignments for the *n*-Alkanes on Pt(111)^a

<i>n</i> -alkane	$\nu(\text{C-H}_{\text{proximal}})$	$\text{CH}_2, \nu(\text{C-H}_{\text{distal}})$	$\text{CH}_3, \nu(\text{C-H}_{\text{distal}})$
propane	2760 (broad)	2912	2936, 2945
butane	2671, 2803	2888 (sh), 2903	2930, 2945
pentane	2683, 2756, 2821	2887, 2905	2928, 2945
hexane	2666, 2752, 2817	2894 (sh), 2903	2928, 2947
heptane	2679, 2758, 2823	2893, 2903	2928, 2947
octane	2669, 2758, 2818	2896 (sh), 2903	2929, 2947
nonane	2683, 2760, 2825	2897 (sh), 2903	2930, 2945
decane	2687, 2760	2900 (broad)	2932, 2944

^a Frequencies are given in cm^{-1} .

leads to the complete exchange of one chain by the other (with C_8D_{18} in direct contact with the surface).³¹

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 shown in 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

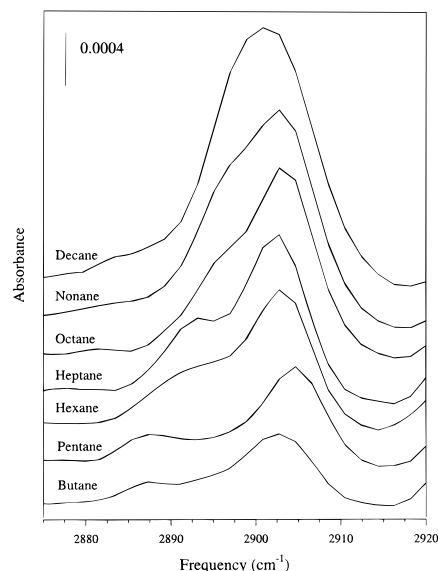


Figure 2. An expansion of Figure 1 illustrating the detail in the vibrational feature at $\sim 2900 \text{ cm}^{-1}$.

C–H methylene bonds (H_d 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 (H_p) that are perturbed by interactions with the surface.² The bands at ~ 2930 and 2945 cm^{-1} arise from in-phase ($\text{H}_b + \text{H}_c$ in the diagram) and out-of-phase ($\text{H}_b - \text{H}_c$) 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 (H_a).

The feature at $\sim 2900 \text{ cm}^{-1}$ 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 $<6 \text{ cm}^{-1}$ 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 ($\theta \cong 0.22\theta_{\text{sat}}$), 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 $\theta_i \cong 1.5\theta_{\text{sat}}$), 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

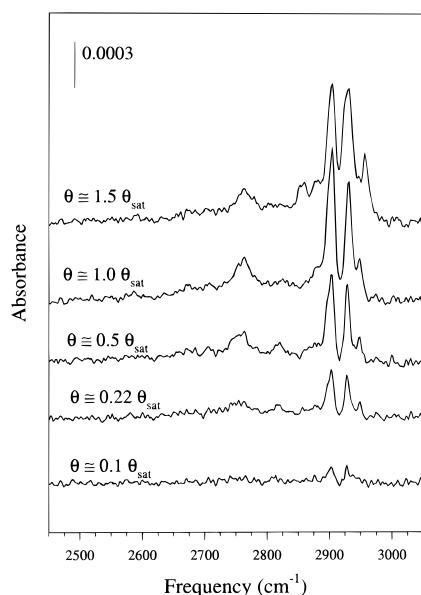


Figure 3. RAIR spectra of *n*-octane on Pt(111) at 110 K as a function of coverage.

TABLE 2: Mode Assignments for Isotopically Labeled *n*-Hexanes on Pt(111)^a

<i>n</i> -alkane	$\nu(\text{C}-\text{H}_{\text{proximal}})$	CH_2 , $\nu(\text{C}-\text{H}_{\text{distal}})$	CH_3 , $\nu(\text{C}-\text{H}_{\text{distal}})$
$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	2666, 2752, 2817	2894 (sh), 2903	2928, 2947
$(\text{CD}_2\text{HCD})_2(\text{CH}_2)_2$	2681, 2751, 2820	2889	2916
$(\text{CH}_3\text{CH}_2)_2(\text{CD}_2)_2$	2735, 2820	2897	2926, 2945

^a Frequencies are given in cm^{-1} .

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 ~ 2855 and 2930 cm^{-1} are the symmetric and antisymmetric stretches, respectively, of the methylene groups while the bands at ~ 2880 and 2960 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) surfaces² have been tested by investigating the RAIR spectra of the isotopically labeled *n*-hexanes $\text{CH}_3\text{CH}_2(\text{CD}_2)_2\text{CH}_2\text{CH}_3$ and $\text{CD}_2\text{HCD}_2(\text{CH}_2)_2\text{CD}_2\text{H}$ (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 cm^{-1} .

Monolayers of unlabeled *n*-hexane and the two labeled hexanes adsorbed onto Pt(111) give the RAIR spectra shown in Figure 4. Particularly informative is a comparison of the RAIR spectra of *n*-C₆H₁₄ and the isotopolog $\text{CH}_3\text{CH}_2(\text{CD}_2)_2\text{CH}_2\text{CH}_3$, which is selectively deuterated at "chain interior" sites. As expected, the C—H_{distal} methyl stretches at ~ 2926 and 2945 cm^{-1} are essentially identical for *n*-C₆H₁₄ and $\text{CH}_3\text{CH}_2(\text{CD}_2)_2\text{CH}_2\text{CH}_3$. The most notable difference between the two spectra is that the feature at $\sim 2900 \text{ cm}^{-1}$ is less intense for the labeled molecule. This finding confirms the previous assignment of this mode to distal C—H methylene stretches. Interestingly, the line shape of the $\sim 2900 \text{ cm}^{-1}$ band for $\text{CH}_3\text{CH}_2(\text{CD}_2)_2\text{CH}_2\text{CH}_3$

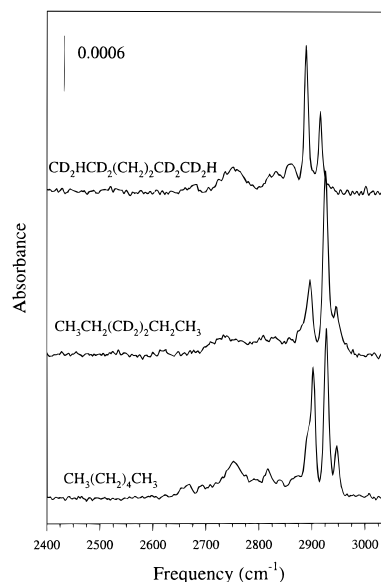


Figure 4. RAIR spectra of saturated monolayers of (top) $\text{CD}_2\text{HCD}_2(\text{CH}_2)_2\text{CD}_2\text{H}$, (middle) $\text{CH}_3\text{CH}_2(\text{CD}_2)_2\text{CH}_2\text{CH}_3$, and (bottom) *n*-C₆H₁₄ on Pt(111). The specified *n*-hexane was dosed while the Pt(111) crystal was held at a temperature above the multilayer desorption threshold but below the monolayer desorption threshold of the adsorbate. The spectra were acquired at 110 K.

CH_3 is asymmetric and (although hard to see on the scale of the figures) apparently still consists of two components. This observation supports the conclusion reached above: the separate components of the 2900 cm^{-1} feature cannot be due to methylene groups at varying distances from the chain termini.

A second difference between the RAIR spectra of *n*-C₆H₁₄ and $\text{CH}_3\text{CH}_2(\text{CD}_2)_2\text{CH}_2\text{CH}_3$ is that the low-frequency mode near 2760 cm^{-1} is less intense for the latter molecule. This finding also confirms that this feature is due to a methylene C—H stretch. A third difference is that the frequency of the softened mode ($\sim 2735 \text{ cm}^{-1}$) is some 15 cm^{-1} lower than that seen for unlabeled *n*-C₆H₁₄, which suggests that the methylene units near the chain ends may have slightly stronger interactions with the surface than do the interior methylene units.

Also informative is the RAIR spectrum of the *n*-hexane isotopolog $\text{CD}_2\text{HCD}_2(\text{CH}_2)_2\text{CD}_2\text{H}$, which is deuterated at the chain ends rather than the chain interior. Most notable is that the C—H_{distal} methylene stretch appears as a single sharp band at 2889 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.

The RAIR spectrum of $\text{CD}_2\text{HCD}_2(\text{CH}_2)_2\text{CD}_2\text{H}$ differs from those of *n*-C₆H₁₄ and $\text{CH}_3\text{CH}_2(\text{CD}_2)_2\text{CH}_2\text{CH}_3$ in one other important respect: the C—H distal methyl stretch appears as a single sharp band at 2916 cm^{-1} rather than as two bands at ~ 2926 and 2945 cm^{-1} . In unlabeled *n*-hexane, the two bands arise from the in-phase and out-of-phase combinations of the two C—H_{distal} bonds. In $\text{CD}_2\text{HCD}_2(\text{CH}_2)_2\text{CD}_2\text{H}$, there is only one C—H bond in each methyl group. If the hydrogen atom occupies site H_c in the diagram above, the transition moment of the C—H stretch will be nearly parallel with the surface and the RAIR intensity will be near zero. The single band at 2916 cm^{-1} must therefore be due to the rotamer in which the lone hydrogen occupies distal site H_b. The presence of only a single hydrogen atom on each methyl group also explains why this band is less intense than the C—H_{distal} methyl stretching bands seen for the other two *n*-hexane isotopologs.

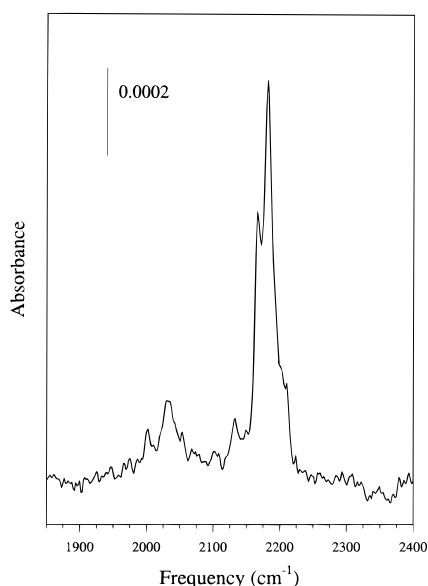


Figure 5. RAIR spectrum of a saturated monolayer of *n*-C₈D₁₈ on Pt(111) at 110 K.

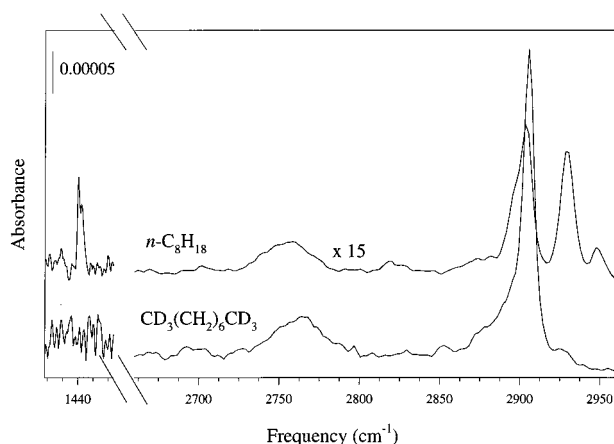


Figure 6. RAIR spectra of saturated monolayers of (top) *n*-C₈H₁₈ and (bottom) CD₃(CH₂)₆CD₃ on Pt(111) at 110 K.

Finally, the RAIR spectrum of CD₂HCD₂(CH₂)₂CD₂CD₂H exhibits a well-defined softened mode at ~ 2760 cm⁻¹ due to the C-H_{proximal} stretching motions of the interior methylene groups. The frequency of this band is very similar to that seen for unlabeled *n*-C₆H₁₄. 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_{proximal} methylene stretches are more intense than those of the chain-end C-H_{proximal} methylene stretches, so that the former dominate the line shape in the spectrum of unlabeled *n*-C₆H₁₄.

RAIR Spectra of Isotopically Labeled *n*-Octanes. We have also investigated the RAIR spectra of two deuterated *n*-octanes: CD₃(CH₂)₆CD₃ and *n*-C₈D₁₈ (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*-C₈D₁₈ 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*-C₈H₁₈. Table 4 summarizes the $\nu_{C-H}:\nu_{C-D}$ ratios for the corresponding vibrational features in the RAIR spectra of *n*-C₈H₁₈ and *n*-C₈D₁₈ 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: $\omega_{C-H}/\omega_{C-D} = (m_{C-D}^*)^{1/2}/(m_{C-H}^*)^{1/2} = 1.36$.

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” ν_{C-D} modes at much lower frequencies. The latter features are direct evidence of surface C–D \cdots M interactions. Softened modes at similar frequencies have also been observed for cyclohexane-*d*₁₂ adsorbed on transition metals.^{19,22} Like *n*-C₈H₁₈, the labeled molecule *n*-C₈D₁₈ gives a softened mode that appears to have structure: a feature at 2020 cm⁻¹ is particularly prominent.

For the partially deuterated *n*-octane CD₃(CH₂)₆CD₃, the two peaks at 2929 and 2947 cm⁻¹ seen for *n*-C₈H₁₈ are completely absent, and this observation confirms that these bands are due to C–H_{distal} stretching motions of the methyl groups (Figure 6). The 2820 cm⁻¹ band seen for *n*-C₈H₁₈ is also absent, and this finding confirms that this feature arises from C–H_{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 ~ 1051 cm⁻¹ in the labeled molecule. The only vibrational features present in the RAIR spectrum of CD₃(CH₂)₆CD₃ above 2600 cm⁻¹ are those that arise from C–H stretches of the methylene groups. The C–H_{proximal} stretching motions give rise to a softened mode at 2766 cm⁻¹ (a frequency identical to that of unlabeled *n*-C₈H₁₈), while the C–H_{distal} stretching motions produce the intense band at 2905 cm⁻¹. Whereas for *n*-C₈H₁₈ the latter band has two distinct components, for CD₃(CH₂)₆CD₃ only a single (albeit asymmetric) component is evident. This observation provides an additional clue to the origin of the splitting seen in *n*-C₈H₁₈ (see below).

Significant changes occur in the organization of a saturated monolayer of CD₃(CH₂)₆CD₃ as the temperature is raised (Figure 7). Particularly notable is that the softened mode centered at ~ 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*-C₈H₁₈. 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*-C₈H₁₈ and CD₃(CH₂)₆CD₃. 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).² The bands at ~ 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_{distal} stretching motions of the methylene groups, and the softened modes at ~ 2760 and 2820 cm⁻¹ arise from the C–H_{proximal} stretching motions of the methylene and methyl groups, respectively. There is also a split band at ~ 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)^a

$n\text{-alkane}$	$\text{CX}_3, \delta(\text{C-X})$	$\nu(\text{C-H}_{\text{proximal}})$	$\text{CH}_2, \nu(\text{C-H}_{\text{distal}})$	$\text{CH}_3, \nu(\text{C-H}_{\text{distal}})$
$n\text{-C}_8\text{H}_{18}$	1441, 1447	2669, 2758, 2818	2896 (sh), 2903	2929, 2947
$\text{CD}_3(\text{CH}_2)_6\text{CD}_3$	1051	2697, 2766	2905	

^a 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)^a**

mode assignment	$n\text{-C}_8\text{D}_{18}$	$n\text{-C}_8\text{H}_{18}$	freq. ratio
methyl distal out-of-phase	2208	2947	1.33
methyl distal in-phase	2181	2929	1.34
methylene distal stretch	2166	2900	1.34
methylene proximal stretch	2033	2758	1.36
methyl bend	1053	1445	1.37

^a Frequencies are given in cm^{-1} .

teration, the bands move by the expected amount to lower frequency (Table 4).

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 $\text{C-H}_{\text{distal}}$ stretches from methylene segments lying at various distances from the chain termini. In fact, different frequencies for the C-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 $\text{CH}_3\text{CH}_2(\text{CD}_2)_2\text{CH}_2\text{CH}_3$ 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 $\text{CD}_2\text{HCD}_2(\text{CH}_2)_2\text{CD}_2\text{H}$, 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 $\text{C-H}:\text{C-D}$ ratio: the $\text{C-H}_{\text{distal}}$ methyl stretching modes at 2929 and 2947 cm^{-1} and the C-H methyl bending mode at $\sim 1445\text{ cm}^{-1}$. Interestingly, twice the frequency of the latter mode ($1445 \times 2 = 2890\text{ cm}^{-1}$) corresponds closely to the frequency observed for the $\text{C-H}_{\text{distal}}$ methylene vibration for $n\text{-C}_8\text{H}_{18}$ ($\sim 2900\text{ cm}^{-1}$). We therefore propose that the two components seen near 2900 cm^{-1} arise from a Fermi resonance between the first overtone of the C-H bend of the methyl groups and the fundamental of the $\text{C-H}_{\text{distal}}$ 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 ($\text{CD}_3(\text{CH}_2)_6\text{CD}_3$) 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 $\text{C-H}_{\text{distal}}$ methylene stretch is essentially independent of the location of the methylene unit within the chain, the frequency of the softened mode due to the $\text{C-H}_{\text{proximal}}$ methylene stretches is $\sim 15\text{ cm}^{-1}$ lower for

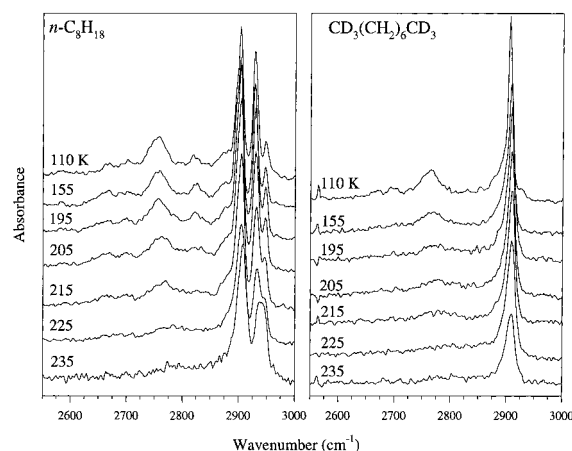


Figure 7. Variable-temperature RAIR spectra of saturated monolayers of (left) $n\text{-C}_8\text{H}_{18}$ and (right) $\text{CD}_3(\text{CH}_2)_6\text{CD}_3$ on Pt(111) at 110 K. Because the desorption of the $n\text{-octanes}$ is significant at 235 and 245 K, the spectra at these temperatures were collected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

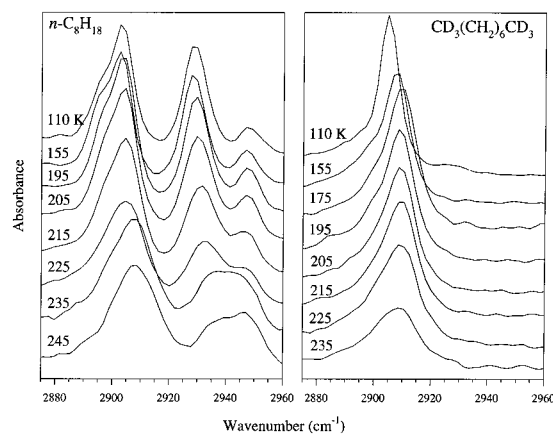


Figure 8. Expanded view of Figure 7 showing the $2875\text{--}2960\text{ cm}^{-1}$ region in more detail.

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 $\text{C-H}_{\text{proximal}}$ and $\text{C-H}_{\text{distal}}$ Stretching Vibrations. As shown in our earlier publication and by Firment and Somorjai, monolayers of $n\text{-hexane}$, $n\text{-octane}$, and $n\text{-decane}$ order 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 $2\text{D} \rightarrow 1\text{D}$ transition is correlated with two changes seen in the infrared spectra: the softened mode at $\sim 2760\text{ cm}^{-1}$ due to the $\text{C-H}_{\text{proximal}}$ methylene stretches begins to move to higher frequency and the band at $\sim 2900\text{ cm}^{-1}$ due to the methylene $\text{C-H}_{\text{distal}}$ stretches begins to broaden.

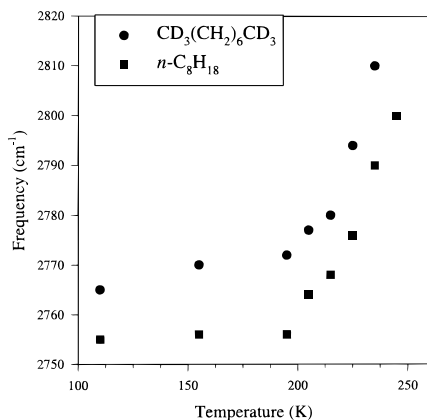


Figure 9. Temperature dependence of the frequency of the softened mode at $\sim 2760\text{ cm}^{-1}$ for $n\text{-C}_8\text{H}_{18}$ (■) and $\text{CD}_3(\text{CH}_2)_6\text{CD}_3$ (●).

The behavior of $\text{CD}_3(\text{CH}_2)_6\text{CD}_3$ 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 $\text{CD}_3(\text{CH}_2)_6\text{CD}_3$, the softened mode at $\sim 2760\text{ cm}^{-1}$ (due to the methylene C–H_{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 \rightarrow 1D phase transition.³ 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 $\text{CD}_3(\text{CH}_2)_6\text{CD}_3$. 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_{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_{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 \cdots M interactions become more prevalent.

Our studies of deuterated n -alkanes, however, do not support our earlier suggestion that the 2D \rightarrow 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 \rightarrow 1D phase transition), the line width increases from ~ 13 to $\sim 20\text{ cm}^{-1}$ at 245 K (Figure 10). In contrast, the single feature near 2900 cm^{-1} seen for $\text{CD}_3(\text{CH}_2)_6\text{CD}_3$ 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

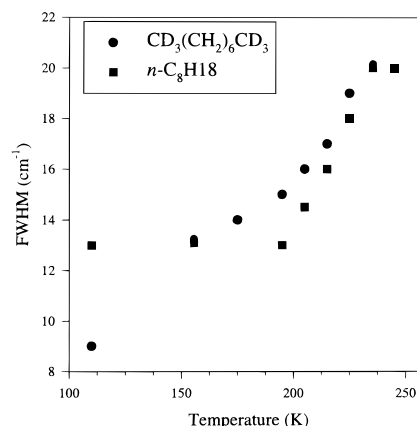


Figure 10. Temperature dependence of the line width of the feature at $\sim 2900\text{ cm}^{-1}$ for $n\text{-C}_8\text{H}_{18}$ (■) and $\text{CD}_3(\text{CH}_2)_6\text{CD}_3$ (●).

is not clear whether the break that occurs in the line width versus temperature curve near the 2D \rightarrow 1D phase transition temperature is coincidental. However, we now feel that the C–H_{distal} methylene oscillators are not sensitive indicators of the underlying order of the overlayer.

The thermodynamics of the structural phase transition 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.^{39,40} 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:

$$\eta = \eta_0(T - T_0)^\beta \quad (1)$$

$$\omega = \omega_0(T - T_0)^{\beta'} \quad (2)$$

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.⁴¹ 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 ω or η is given by a critical exponent, β , 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

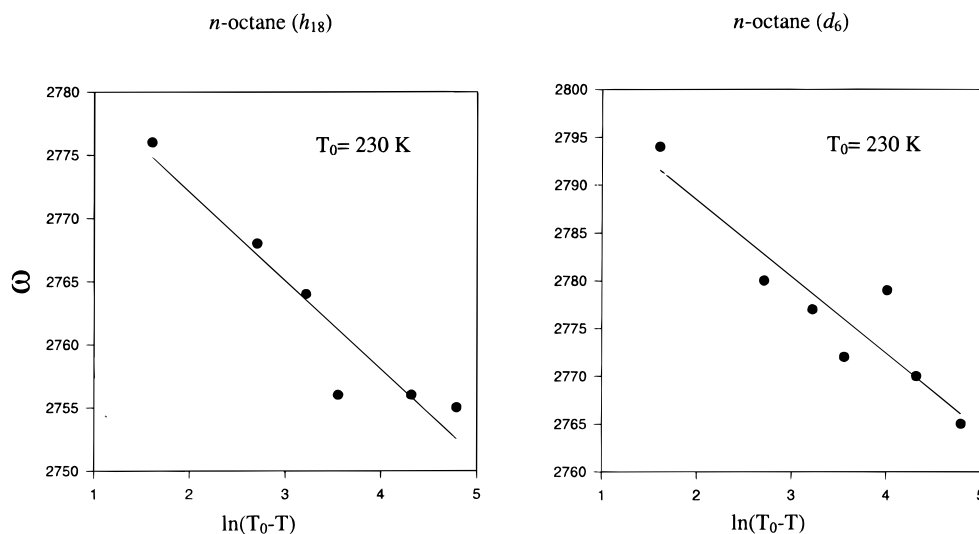


Figure 11. Plots showing the temperature scaling of the CH₂ (proximal), or softened mode frequencies, plotted as $\omega = c(T_0 - T)^\beta$. The ν_{C-H} softened modes for both *n*-octane and the isotopomer CD₃(CH₂)₆CD₃ are shown.

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 ν_{C-H} modes of *n*-octane and the isotopomer CD₃(CH₂)₆CD₃. The linear correlation of the frequencies with $\ln(T_0 - T)$ 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 \rightarrow 1D phase transition. By way of reference, Wöll et al. have characterized and assigned a frustrated translational mode for a closely related *n*-alkane ordered layer on Cu(111); this mode occurs at ~ 52 cm⁻¹ (at 93 K). This mode is not directly related to an adsorbate 2D \rightarrow 1D phase transition, however, as it is polarized along the surface normal direction.^{42,43} 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.⁶

As noted above the mode softening seen in the C–H stretching region reflects the nature (and strength) of the C–H \cdots 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.^{44–47}

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 \cdots 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

- (1) Sikes, H. D.; Schwartz, D. K. *Science* **1997**, *278*, 1604–1607 and references therein.
- (2) Hostettler, M. J.; Manner, W. L.; Nuzzo, R. G.; Girolami, G. S. *J. Phys. Chem.* **1995**, *99*, 15269–15278.
- (3) Firment, L. E.; Somorjai, G. A. *J. Chem. Phys.* **1977**, *66*, 2901–2913.
- (4) Raut, J. S.; Fichthorn, K. A. *J. Chem. Phys.* **1998**, *108*, 1626–1635.
- (5) Wang, J.-C.; Fichthorn, K. A. *J. Chem. Phys.* **1998**, *108*, 1653–1663.
- (6) Raut, J. S.; Sholl, D. S.; Fichthorn, K. A. *Surf. Sci.* **1997**, *389*, 88–102.
- (7) Kosterlitz, J. M.; Thouless, D. J. *J. Phys. C* **1973**, *6*, 1181–1203.
- (8) Nelson, D. R.; Halperin, B. I. *Phys. Rev. B* **1979**, *19*, 2457–2484.
- (9) Zippelius, A.; Halperin, B. I.; Nelson, D. R. *Phys. Rev. B* **1980**, *22*, 2514–2541.
- (10) Young, A. P. *Phys. Rev. B* **1979**, *19*, 1855–1866.
- (11) Hansen, F. Y.; Newton, J. C.; Taub, H. *J. Chem. Phys.* **1993**, *98*, 4128–4141.
- (12) Hansen, F. Y.; Taub, H. *Phys. Rev. Lett.* **1992**, *69*, 652–655.
- (13) Demuth, J. E.; Ibach, H.; Lehwald, S. *Phys. Rev. Lett.* **1978**, *40*, 1044–1047.
- (14) Avery, N. R. *Surf. Sci.* **1985**, *163*, 357–368.
- (15) Chesters, M. A.; Parker, S. F.; Raval, R. *J. Electron. Spectrosc. Related Phenom.* **1986**, *39*, 155–162.
- (16) Chesters, M. A.; Gardner, P. *Spectrochim. Acta* **1990**, *46A*, 1011–1015.
- (17) Hostettler, M. J.; Nuzzo, R. G.; Girolami, G. S.; Dubois, L. H. *J. Phys. Chem.* **1994**, *98*, 2952–2962.
- (18) Manner, W. L.; Hostettler, M. J.; Girolami, G. S.; Nuzzo, R. G. *J. Phys. Chem.*, in press.
- (19) Raval, R.; Pemble, M. E.; Chesters, M. A. *Surf. Sci.* **1989**, *210*, 187–200.
- (20) Raval, R.; Chesters, M. A. *Surf. Sci. Lett.* **1989**, *219*, L505.
- (21) Raval, R.; Parker, S. F.; Chesters, M. A. *Surf. Sci.* **1993**, *289*, 227–236.
- (22) Hoffmann, F. M.; Felner, T. E.; Thiel, P. A.; Weinber, W. H. *Surf. Sci.* **1983**, *130*, 173–190.

- (23) Land, D. P.; Erley, W.; Ibach, H. *Surf. Sci.* **1993**, 289, 237–246.
- (24) Weldon, M. K.; Uvdal, P.; Friend, C. M.; Wiegand, B. C. *Surf. Sci.* **1996**, 355, 71–84.
- (25) Firment, L. E.; Somorjai, G. A. *J. Chem. Phys.* **1978**, 69, 3940–3952.
- (26) 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.
- (27) Wiegand, B. C.; Lohokare, S. P.; Nuzzo, R. G. *J. Phys. Chem.* **1993**, 97, 11553–11562.
- (28) Morandi, J. R.; Jensen, H. B. *J. Org. Chem.* **1969**, 34, 1889–1891.
- (29) Birch, A. J.; Walker, K. A. M. *J. Chem. Soc. C* **1966**, 1894–1896.
- (30) Dolivo, G.; Lund, A. Z. *Naturforsch., A: Phys.* **1985**, 40A, 52–65.
- (31) Bishop, A. R.; Hostetler, M. J.; Girolami, G. S.; Nuzzo, R. N. *J. Am. Chem. Soc.* **1998**, 120, 3305–3315.
- (32) Greenler, R. G. *J. Chem. Phys.* **1966**, 44, 310–315.
- (33) Francis, S. A.; Ellison, A. H. *J. Opt. Soc. Am.* **1959**, 49, 131–138.
- (34) Ibach, H.; Mills, D. L. *Electron Energy Loss Spectroscopy of Molecules on Surfaces*; Academic: New York, 1982.
- (35) Sebastian, K. L. *J. Phys. C* **1980**, 13, L115–L117.
- (36) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 3rd ed.; Chapman and Hall: New York, 1975; Vol. 1.
- (37) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic: New York, 1991.
- (38) Snyder, R. G.; Aljibury, A. L.; Strauss, H. L. *J. Chem. Phys.* **1984**, 81, 5352–5361.
- (39) Iqbal, Z.; Owens, F. J. *Vibrational Spectroscopy of Phase Transitions*; Academic Press: Orlando, FL, 1984.
- (40) Scott, J. F. *Rev. Mod. Phys.* **1974**, 46, 83–127 and references therein.
- (41) Raman, C. B.; Nedungadi, T. M. K. *Nature (London)* **1940**, 145, 147.
- (42) Woll, C.; Witte, G. *J. Chem. Phys.* **1995**, 103, 5860–5863.
- (43) Fuhrmann, D.; Woll, C. *Surf. Sci.* **1997**, 377–379, 544–550.
- (44) Ryberg, R. *Phys. Rev. B* **1989**, 40, 8567–8569.
- (45) Ariyasu, J. C.; Mills, D. L.; Lloyd, K. G.; Hemminger, J. C. *Phys. Rev. B* **1984**, 30, 507–518.
- (46) Persson, B. N. J. *J. Phys. C: Solid State Phys.* **1984**, 17, 4741–4750.
- (47) Graham, A.; Hoffmann, F.; Toennies, J. P. *J. Chem. Phys.* **1996**, 104, 531–5316.