

## Fundamental Studies of Hydrocarbon Organization and Reactivity on Platinum Surfaces

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Final Seminar

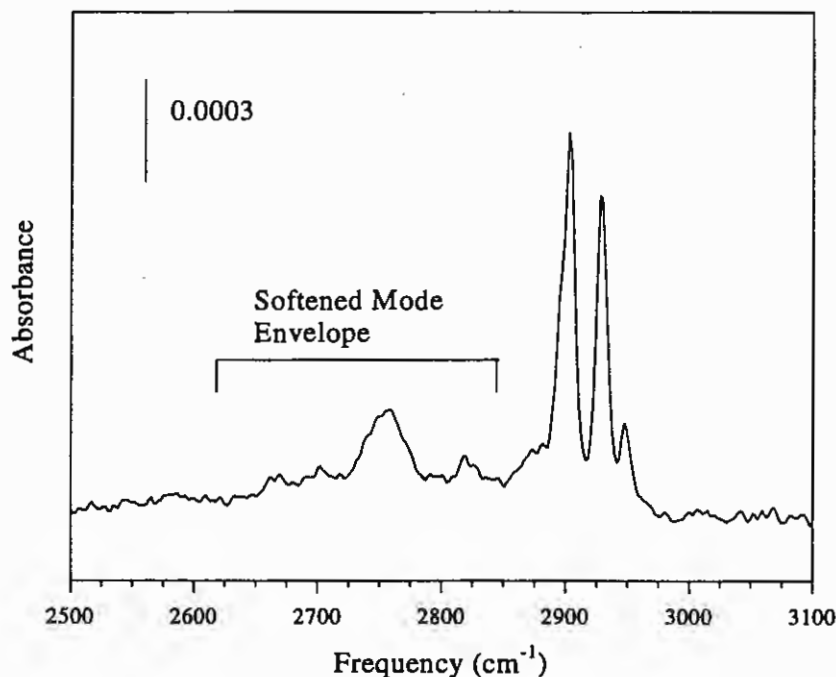
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The strength of the interaction occurring between a hydrocarbon and a metal substrate is a major determinant of the molecular organization and its reactivity. In many cases, the strength of the adsorbate-substrate interaction can be divided into two general classes: physisorption and chemisorption.

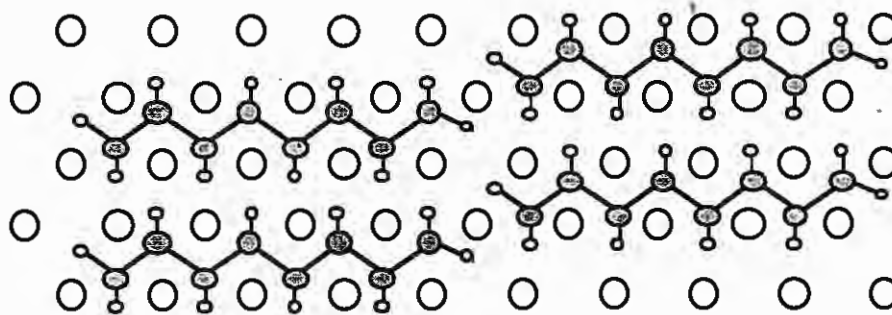
Physisorption is commonplace for saturated hydrocarbons (both linear and cyclic) on many metal surfaces.<sup>1</sup> Despite the weak nature of the adsorbate-substrate interaction seen for these systems, we observe that there are large perturbations to certain C-H bonds due to significant C-H...M interactions. These perturbations are manifested in a typical reflection-absorption infrared (RAIR) spectrum by large red shifts of certain C-H stretching modes (usually referred to as "softened modes").<sup>2,3</sup> Spectroscopic indicators of the perturbed C-H bonds for adsorbed monolayers of *n*-alkanes on Pt(111) (see Figure 1)<sup>4</sup> exhibit linewidths that are very narrow when compared to those seen for cyclic hydrocarbons on this same substrate (FWHMs of 50 vs. 150 cm<sup>-1</sup>, respectively). We have convincingly illustrated that the line width of the softened mode(s) observed for monolayers of the *n*-alkanes (and other hydrocarbon systems) on Pt(111) is largely related to site bonding heterogeneity. Narrow softened modes (structured envelope with an intense feature at ~2760 cm<sup>-1</sup>) for monolayers of *n*-alkanes on Pt(111) are observed for three reasons: first, there is a registry of the adsorbate on the surface, second, the octane overlayers order on the surface, and, third, the adsorbates have a small degree of conformational, rotational, or translational disorder (Figure 2).<sup>5</sup>

Since the nature of the softened mode is acutely sensitive to the disorder present in an *n*-alkane monolayer, we use it as a spectroscopic indicator to monitor phase transitions occurring in monolayers of *n*-hexane, *n*-octane, and *n*-decane on Pt(111). RAIRS data convincingly illustrates that these systems undergo two phase transitions involving reversible two-dimensional to one-dimensional (order-order) and one-dimensional to disordered transformations. Our results are consistent with theory that predicts that the melting of physisorbed monolayers does not have to be a single discontinuous transition; rather, there can exist an intermediate phase whose properties are between those of the ordered solid and the disordered liquid and that the melting of a monolayer can be *continuous*.<sup>6-9</sup>

With chemisorption, the adsorbate-substrate strength of the interactions are much greater than those manifested in physisorbed systems. As a consequence, most hydrocarbon overlayers will react rather than desorb upon thermal treatment; unsaturated cyclic hydrocarbons adsorbed on Pt(111) were shown to dehydrogenate/hydrogenate and/or undergo C-C bond scission.<sup>10-17</sup> The nature of the reactions occurring at higher temperatures and the thermolysis products they generate provide important insights into the processes relevant to heterogeneous catalysis.

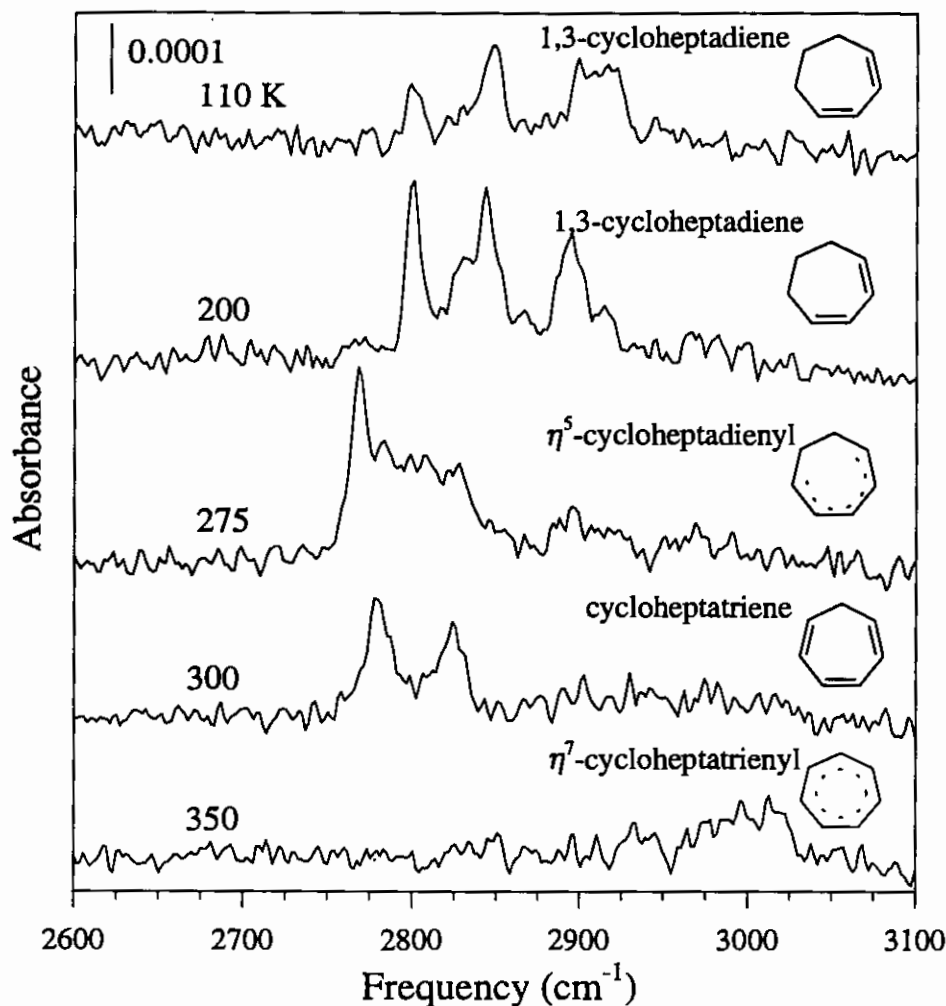


**Figure 1.** Reflection-absorption infrared spectrum for a monolayer of *n*-octane on Pt(111).



**Figure 2.** Proposed disposition of *n*-octane molecules adsorbed on a Pt(111) surface.

Using a combination of temperature-programmed reaction (TPR) and RAIR spectroscopies, we have identified various reaction intermediates of the unsaturated cyclic hydrocarbons ( $C_5$ - $C_8$ ) formed as a function of the temperature. The thermal chemistry of 1,3-cycloheptadiene on Pt(111) provides an illustrative example of the reaction intermediates identified spectroscopically in this work. Shown in Figure 3 are the RAIR spectra for a monolayer of 1,3-cycloheptadiene on Pt(111) along with the reaction intermediates formed as a function of temperature. The appearance of new bands (and the disappearance of others) marks the formation of these intermediates. The identification of these intermediates was further assisted by analyzing the C/H stoichiometries of the surface-bound species by TPRS.



**Figure 3.** Reflection-absorption infrared spectra for a monolayer of 1,3-cycloheptadiene adsorbed on Pt(111) taken after annealing at the listed temperatures.

Our studies revealed that various types of electronic perturbations occur to the C-H bonds of the hydrocarbons upon adsorption on Pt(111). Not only do we observe the aforementioned "mode softening" due to C-H...M but also we observe that some unsaturated cyclic hydrocarbons exhibit unusually low-frequency C-H stretches due to hyperconjugation. These latter bands appear between 2700 and 2800  $\text{cm}^{-1}$  and are much narrower than those arising from C-H...M interactions. An example of this hyperconjugation effect is seen for  $\eta^5$ -cycloheptadienyl formed from the thermolysis of 1,3-cycloheptadiene (the mode appearing at  $\sim 2770 \text{ cm}^{-1}$ , see Figure 3 at 275 K).

Interestingly, all the unsaturated cyclic hydrocarbons dehydrogenate to some extent to form planar intermediates in varying yields:

- cyclopentene and 1,3-cyclopentadiene form a pentahaptopentadienyl ( $\eta^5\text{-Cp}$ ) intermediate;
- cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene form benzene;
- cycloheptene, 1,3-cycloheptadiene, and 1,3,5-cycloheptatriene form a heptahaptoheptatrienyl intermediate;
- *cis*-cyclooctene, *cis,cis*-1,3-cyclooctadiene, 1,5-cyclooctadiene, and 1,3,5,7-cyclooctatetraene form a pentalenyl intermediate.

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