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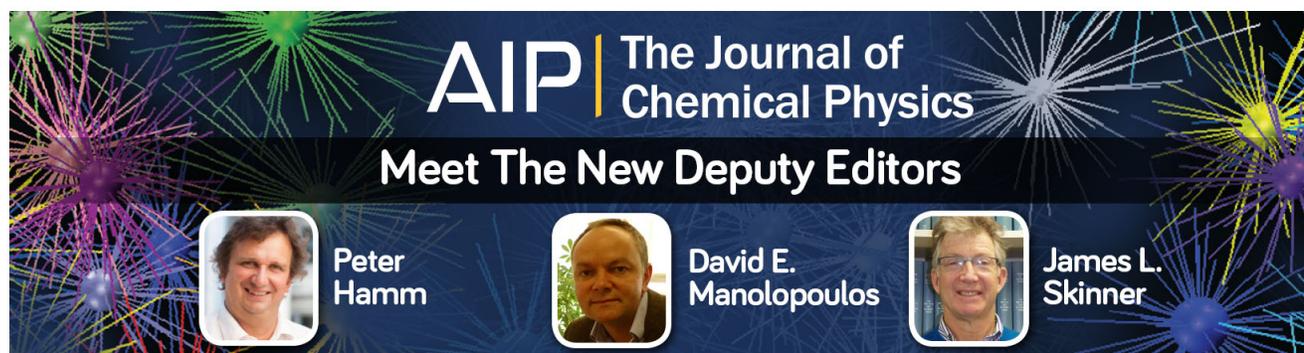
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Softened C–H modes of adsorbed methyl and their implications for dehydrogenation: An *ab initio* study

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To investigate the softening of CH vibrational frequencies and their implications for dehydrogenation of adsorbed hydrocarbons, an issue of scientific and technological importance, density functional theory calculations have been performed on the chemisorption and dehydrogenation of CH₃ on Cu(111) and Pt(111) surfaces. By comparing these results with those of Ni(111) we find that the CH bonds of the adsorbate, when close enough, interact with metal atoms of the surface. It is this interaction and its associated lengthening and weakening of CH bonds that is the physical origin of mode softening. We rule out the possibility of a relationship between the mere presence of mode softening and dehydrogenation. We do show, however, that there is a clear relationship between the extent to which a surface *can* induce mode softening and the activation energy to dehydrogenation. In addition, periodic trends concerning the extent of mode softening are reproduced. © 2001 American Institute of Physics. [DOI: 10.1063/1.1345907]

The interaction and reaction of hydrocarbon adsorbates with metal surfaces is of fundamental scientific and technological importance. Adsorbed hydrocarbons are often observed to exhibit CH stretching modes which are redshifted by several hundred wave numbers below a typical value of $\sim 2900\text{ cm}^{-1}$.¹⁻⁴ The extent of CH mode “softening” is substrate dependent. For hydrocarbons in general it increases along the series Cu<Ni<Pt<Ru. Thus, it is believed to vary periodically, increasing from right to left and from top to bottom. For methyl (CH₃) chemisorption, however, when CH₃ is chemisorbed on Ni(111) and Cu(111) surfaces a softened CH vibration is observed; on Pt(111) and Ru(0001) surfaces, the frequency of the vibration is within 50 cm^{-1} of its gas phase value and usually considered not to be softened.⁵ This appears to be inconsistent with the general trend: The two metals (Pt and Ru) which induce the greatest mode softening in other hydrocarbons have no effect on the CH vibrational potential of adsorbed CH₃. Explanations for this redshift in vibrations have been many and varied.¹⁻⁸ Furthermore, it has been debated that such softened vibrations affect the tendency of the adsorbate to undergo the crucial chemical process of dehydrogenation.^{1,2,7,9}

In this communication, we present the results of density functional theory (DFT) calculations in an attempt to provide a theoretical description of the key experimental observations pertaining to the softening of CH stretching vibrations in adsorbed hydrocarbons. Having examined CH₃ chemisorption and dehydrogenation on Cu(111) and Pt(111), augmented with our previous results on Ni(111), we aim to (i) explain the presence/absence and extent of mode softening on different metals and (ii) determine if there is indeed a relationship between mode softening and the proclivity of an adsorbed hydrocarbon to dehydrogenate.

DFT calculations using ultrasoft pseudopotentials¹⁰ within a plane wave basis set¹¹ were performed for CH₃ on Cu(111) and Pt(111). Exchange and correlation effects are described by the PW-91 generalized gradient approximation.¹² A Monkhorst-Pack mesh with $2\times 2\times 1$ **k**-point sampling, within the surface Brillouin zone, was found to offer sufficient accuracy.^{13,14} The Pt and Cu surfaces are modeled by a periodic array of slabs. A large $p(3\times 2)$ surface unit cell is used. Each slab consists of three layers of metal atoms fixed at bulk truncated positions. Testing calculations were conducted using a four-layer slab in which the top layer of surface atoms was allowed to relax. Reaction barriers between this and the chosen model differed by $<0.1\text{ eV}$, and reaction pathways and transition states were similar. The surface degrees of freedom were found to play only a minor role in the overall reactivity. In addition, previous studies using this and similar models have shown that this approach provides a satisfactory description of the adsorbate-substrate interface.¹⁵ Reaction pathways were determined using a method similar to one previously reported.¹⁶ Transition states were searched by constraining the distance between C and the active H of CH₃ and minimizing the total energy with respect to all remaining degrees of freedom. This method allows the reaction complex to rotate and translate subject to the above constraint. The transition state is identified when (i) the forces on the atoms vanish and (ii) the energy is a maximum along the reaction coordinate but a minimum with respect to all remaining degrees of freedom.

In order to determine the preferred chemisorption site for CH₃ on Cu(111) and Pt(111), structure optimizations were performed at each of the four high-symmetry sites, i.e., top, bridge, and fcc and hcp threefold hollow sites. Chemisorption energies for CH₃ at each site on both surfaces are listed in Table I. To compare these results with previous ones,⁸ chemisorption energies of CH₃ on Ni(111) are also shown in the table. It can be seen that the threefold hollow sites are the

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TABLE I. Chemisorption energies in eV for CH₃ chemisorbed at the high symmetry sites of Cu(111), Pt(111), and Ni(111).

	Fcc	Hcp	Bridge	Top	Expt. ^a
Cu(111)	1.57	1.56	1.47	1.35	1.43 ± 0.35
Pt(111)	1.38	1.25	1.39	2.05	
Ni(111) ^b	1.46	1.48	1.37	1.22	

^aThe only available experimental value for the CH₃ chemisorption energy on a metal surface is for CH₃ on Cu(110) (Ref. 4).

^bReference 8.

preferred chemisorption sites for CH₃ on Cu(111); while on Pt(111), the top site is favored. This is consistent with the general consensus that CH₃ binds to threefold hollow sites on Cu(111) and top sites on Pt(111).^{3,17,18} On Ni(111) CH₃ binds most strongly to the surface at threefold hollow sites.^{5,6,8}

Table II lists redshifts of calculated and experimental CH symmetric stretch vibrations for CH₃ on Cu(111), Pt(111), and Ni(111).¹⁹ Agreement between calculated and experimental shifts is good. Calculations reveal that when CH₃ is adsorbed at fcc sites on Cu, Ni, and Pt, the CH symmetric stretch is softened substantially, by >130 cm⁻¹. Since the CH bond lengths of adsorbed CH₃ are similar at both hcp and fcc sites and because CH bond length is related to CH stretch frequency (see below) it is likely that CH₃ will experience a similar extent of mode softening when adsorbed at the hcp sites as it does at the fcc sites. Calculations also reveal that when CH₃ is adsorbed at top sites, however, no significant (<50 cm⁻¹) mode softening is observed. Therefore, the presence or absence of a softened vibration of CH₃ is simply a consequence of the site at which it is chemisorbed. Softened vibrations are observed experimentally for CH₃ on Ni(111) and Cu(111) because threefold hollow sites are preferred on these surfaces, while a softened vibration is not observed for CH₃ on Pt(111) since the top site is the favored chemisorption site on this surface. It should be stressed that if CH₃ were to adsorb at threefold hollow sites on Pt(111), it would exhibit a softened CH stretch mode (Table II). It is possible, therefore, to distinguish between CH₃ chemisorption at threefold hollow sites and top sites from the presence or absence of mode softening in its vibrational spectrum. The absence of a softened mode for CH₃ on Ru(0001), for example, clearly points to the top site as the preferred chemisorption site for CH₃ on this surface. This was speculated recently by Sheppard and de la Cruz.³

TABLE II. Calculated and experimental redshifts in CH symmetric stretch vibrational frequencies (cm⁻¹) and selected structural parameters for CH₃ chemisorbed on Pt(111), Cu(111), and Ni(111).

Site	Cu(111)		Pt(111)		Ni(111) ^a	
	Fcc	Top	Fcc	Top	Fcc	Top
Redshift	137	50	293	42	267 ^c	
$\nu(\text{CH})_s$ calc. ^b						
Redshift	127			32	262	
$\nu(\text{CH})_s$ expt. ^b						
C-H(Å)	1.097	1.088	1.105	1.090	1.101	1.093
C-metal(Å)	2.227	2.005	2.336	2.103	2.278	2.007
H-metal(Å)	2.123	2.572	2.171	2.649	2.214	2.589

^aReference 8.

^bFrequency shifts upon adsorption are estimated with reference to values of 2997 cm⁻¹ (calculated) and 2917 cm⁻¹ (experimental) for the CH symmetric stretch of CH₄.

^cValue determined by subtraction of calculated value of 2730 cm⁻¹ (Ref. 19) from calculated CH₄ value (2997 cm⁻¹).

Why is the CH symmetric stretching vibration softened when CH₃ is adsorbed at hollow sites and not at top sites? The answer to this question centers upon the fact that when CH₃ is adsorbed at threefold hollow sites short H-metal distances (Table II) allow for the CH bonds of CH₃ to interact with the underlying surface. A quantum state analysis reveals that this interaction is essentially a mixing of **e1** CH bonding orbitals of CH₃ with **d** states of the surface.⁸ The interaction, which is the physical origin of mode softening, lengthens slightly (Table II) and weakens the CH bonds of CH₃ when adsorbed at hollow sites. When CH₃ is adsorbed at top sites the H-metal distances are longer (Table II) and the CH-metal interaction is weaker. The CH bonds of CH₃ when adsorbed at top sites are only slightly elongated and consequently the vibrational frequency experiences a much smaller (negligible) shift. We see, in fact, that the length of a CH bond is related to the extent of mode softening it experiences. Figure 1(a) shows a plot of CH bond length against calculated vibrational frequency for CH₃ adsorbed on Cu, Pt, and Ni. It is seen that as the CH bond length increases, the frequency of the CH symmetric stretch decreases.

Of further interest is the extent to which a CH vibration is softened by different surfaces. If a surface induces mode softening in an adsorbate, then the extent to which it does so is similar for different adsorbates. On Cu(111), for example, CH modes of cyclohexane and CH₃ are both redshifted by ~130 cm⁻¹.^{2,3} For certain hydrocarbons the extent of mode

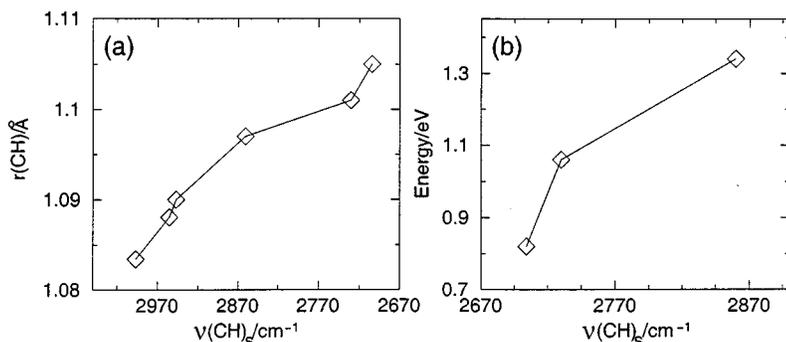


FIG. 1. (a) Relationship between the calculated CH symmetric stretch and CH bond length of chemisorbed CH₃ on the fcc and top sites of Cu(111), Pt(111), and Ni(111). (b) Relationship between the calculated CH symmetric stretch and the activation energy for CH₃ dehydrogenation on Cu(111), Ni(111), and Pt(111).

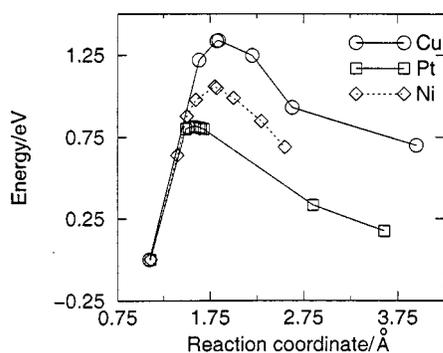


FIG. 2. Energy profile in eV for CH_3 dehydrogenation on Cu(111), Pt(111), and from Ref. 13 Ni(111).

softening is found to vary periodically, increasing from right to left and from top to bottom. The metals of the present study, augmented with Ni, allow us to investigate this. From Table II it is seen that the calculated redshifts in the CH symmetric stretch of CH_3 are 137, 267, and 293 cm^{-1} at the fcc threefold hollow sites of Cu, Ni, and Pt, respectively. This indicates that if the adsorption site were the same on all three surfaces, then the Pt surface *would* induce the greatest mode softening and that the extent of mode softening would increase from $\text{Cu} \rightarrow \text{Ni} \rightarrow \text{Pt}$. Thus our calculations are consistent with both periodic trends.

It has been suggested that the presence of mode softening in an adsorbate may lower the activation energy to CH bond rupture.^{1,2,7,9} This is a crucial issue which affects the stability and reactivity of the adsorbed hydrocarbon. In order to determine the effect of both the presence and extent of mode softening on dehydrogenation of an adsorbed hydrocarbon, we have determined the reaction pathway and activation energy for the dehydrogenation of CH_3 to CH_2 on both Cu and Pt:



The energy profile and reaction pathway for each reaction are shown in Figs. 2 and 3, respectively. For reference our energy profile for CH_3 dehydrogenation on Ni(111)¹³ is also included in Fig. 2.

The most stable adsorption sites for CH_3 on Cu(111) and Pt(111) are the initial states for CH_3 dissociation on these surfaces [Fig. 3(a)]. On Pt(111) it is found that as one of the C–H bonds of CH_3 is stretched the CH_3 moiety diffuses from its initial top site to a bridge site. On Cu(111), however, CH_3

remains quite close to the fcc site as one of its C–H bonds is stretched. At the transition states of the reaction on each surface the CH_3 is highly distorted with a C–H distance of 1.84 and 1.63 Å on Cu and Pt, respectively [Fig. 3(c)]. After the transition states, the nascent H– CH_2 species relax to produce the most stable coadsorption structure of $\text{CH}_2 + \text{H}$ in $p(3 \times 2)$ unit cells on Cu(111) and Pt(111) [Fig. 3(d)]. Both CH_3 dissociation pathways differ from that previously determined on Ni(111).¹³

The activation energies for CH_3 dehydrogenation on Cu(111) and Pt(111) are 1.34 and 0.83 eV, respectively. These barriers agree well with the temperatures at which CH_3 become thermally activated on Cu(111) and Pt(111).^{20,21} The reaction barrier for CH_3 dissociation on Ni(111) has previously been determined to be 1.06 eV.¹³ A consideration of each of these yields some interesting results. First, for chemisorbed CH_3 it is clear that there is no relationship between the mere presence of a softened vibration and the barrier to dehydrogenation. As has been shown, Ni and Cu surfaces both induce softened vibrations in chemisorbed CH_3 , while Pt does not. Yet the barriers for the dehydrogenation of CH_3 on both Cu (1.34 eV) and Ni (1.06 eV) are larger than the barrier to dehydrogenation on Pt (0.82 eV). Second, and more important, there is a clear relationship between the extent to which a surface *can* induce mode softening in an adsorbed species and the reaction barrier to dehydrogenation. In Fig. 1(b) the activation energies for the dehydrogenation of CH_3 on Cu, Ni, and Pt are plotted against the CH vibrational frequency of CH_3 chemisorbed at the same site (fcc hollow site) on each surface. It is clear that the extent of mode softening is inversely proportional to the barrier to dehydrogenation. We show, therefore, for the first time, that the greater the extent to which a surface *can* induce mode softening in an adsorbed hydrocarbon, the lower the barrier to dehydrogenation on that surface. The extent of mode softening in an adsorbate clearly measures the ability of the surface to break the CH bonds of that adsorbate.

In conclusion, if an adsorbate chemisorbs in such a way that its CH bonds are in close proximity to the surface (for CH_3 this occurs at hollow sites), then softened modes will be observed. We rule out the possibility of a relationship between the mere presence of mode softening and dehydrogenation. There is, however, a clear relationship between the extent to which a surface *can* induce mode softening and the activation energy to dehydrogenation.

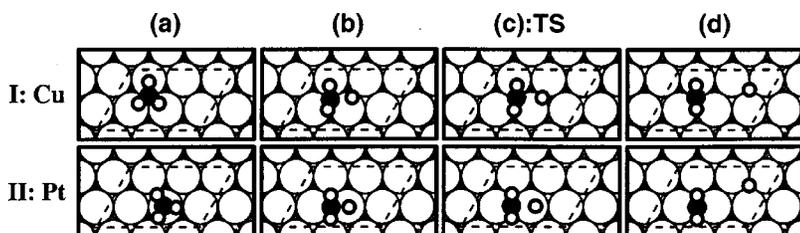


FIG. 3. Lowest energy reaction pathways identified for CH_3 dehydrogenation to CH_2 and H on Cu(111) (I) and Pt(111) (II). Panels (a), the initial states, are the most stable adsorption structures of CH_3 on Cu(111) and Pt(111). Panels (c) illustrate the transition states for both reactions. Panels (d) are the final states of the reactions and correspond to the most stable coadsorptions of CH_2 and H within $p(3 \times 2)$ unit cells on Cu(111) and Pt(111). The dashed lines represent the surface unit cell. For clarity the periodic nature of the systems is not shown.

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