[1] J. Meyer and G. v. Minnigerode, Phys. Lett. 38A, 529 (1972); J. D. Meyer, Appl. Phys. 2, 303 (1973); J. D. Meyer and R. Tidecks, Solid State Commun. 18, 305 (1976).

[2] J. Meyer and R. Tidecks, Solid State Commun. 24, 639, 643 (1977).

[3] W. J. Skocpol, M. R. Beasley, and M. Tinkham, J. Low Temp. Phys. 16, 145 (1974).

[4] A similar effect is observed for two closely spaced short microbridges: J. E. Mooij, private communication.

[5] L. Kramer and A. Baratoff, Phys. Rev. Lett. 38, 518 (1977), and to be published.

[6] Recent experiments on extremely thin and homogeneous tin wires drawn out of a jet pipe support this result: R. Doll and R. Meier-Hirmer, private communication.

[7] A. I. Larkin and Yu N. Ovchinnikov, Zh. Eksp. Teor. Fiz. 73, 299 (1977) [Sov. Phys. JETP (to be published)]; Yu N. Ovchinnikov, J. Low Temp. Phys. 28, 43 (1977).

[8] A. Schmid and G. Schön, J. Low Temp. Phys. 20, 207 (1975).

[9] K.-D. Usadel, Phys. Rev. Lett. 25, 507 (1970).

[10] U. Eckern and G. Schön, to be published.

[11] A. A. Golub, Zh. Eksp. Teor. Fiz. 71, 341 (1976) [Sov. Phys. JETP 44, 178 (1976)].

[12] G. J. Dolan and L. D. Jackel, Phys. Rev. Lett. 39, 1628 (1977).

CH Vibration Softening and the Dehydrogenation of Hydrocarbon Molecules on Ni(111) and Pt(111)

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High-resolution electron energy-loss measurements of ethylene on Ni(111) and cyclohexane on Ni(111) and Pt(111) show an extra CH stretching vibration—not found in free molecules or organometallic compounds—which is strongly broadened and shifted to lower frequencies relative to another, more typical CH stretching vibration. This softened and broadened CH frequency is attributed to a new electronic interaction with the surface which we relate to the mechanism of hydrocarbon dehydrogenation.

Despite many recent advances in understanding the bonding of atoms and molecules to surfaces[1-3] and experimentally determining reaction products on surfaces,[2,3] little information exists regarding the physical mechanisms for surface reactions. Of the only detailed studies to investigate molecular reaction mechanisms, namely the dissociative adsorption of methane on W[4] and Rh,[5] the mechanism is disputed.

Here, we report new results which provide evidence that vibrational spectroscopy permits the detection of changes in vibrational potentials which are important to the chemical transformation of molecules on surfaces, and that suggest a specific interaction mechanism for dehydrogenation reactions. Namely, using high-resolution electron energy-loss spectroscopy, we observe that adsorbed ethylene on Ni(111) and cyclohexane on either Ni(111) or Pt(111) show two sets of CH stretching frequencies. One frequency (2900–3000 cm^{-1}) is reasonable for CH stretching vibrations as found in free molecules,[6] adsorbed hydrocarbons,[3,7] or organometallic compounds,[8] while the second CH frequency (2590–2720 cm^{-1}) is unusually low and broadened by 200–300 cm^{-1}. This latter CH stretching frequency and frequency broadening have not been observed previously[3,6-8] and appear to be directly related to the ability of these particular molecules to dehydrogenate on the surface at higher temperature tures.

We present evidence that this CH vibration softening and broadening arise from an electronic interaction between some of the molecule's hydrogen atoms and the surface, similar to that occurring in hydrogen bonding. We postulate that this interaction not only modifies the shape of the CH vibrational potential but also lowers the activation barrier to CH bond rupture so as to make dehydrogenation the preferred reaction path at higher temperatures. Such a surface interaction has not been detected by other techniques and may provide a physical basis for understanding other chemical reactions on surfaces.

Electron energy-loss spectroscopy (ELS) was performed with a two-stage analyzer/monochromator which typically allows 65–80-cm^{-1} (8–10 meV) energy resolution and provides a low, uniform background as described elsewhere.[3] The choice of primary beam energy and (total) scattering angles did not affect these results and typical values, 5 eV/140° and 4.2 eV/160° for Pt and Ni, were chosen to optimize the loss signal. The Ni(111) and Pt(111) samples were prepared in a similar fashion, separately mounted on a liquid-nitrogen-cooled manipulator ($T_{\rm min}=140$ K), and cleaned using standard methods.[3,2] The systems pressures were typically 1×10^{-10} Torr during measurements; however, after cooling the sample to low temperatures some traces of residual contaminants were occasionally observed on the surfaces. Surface cleanliness and ordering were monitored by Auger electron spectroscopy and LEED (low-energy electron diffraction), respectively. The vapors of reagent-grade cyclohexane and high-purity ethylene (99.95%) and their deuterated counterparts were used and examined for impurities by mass spectroscopy.

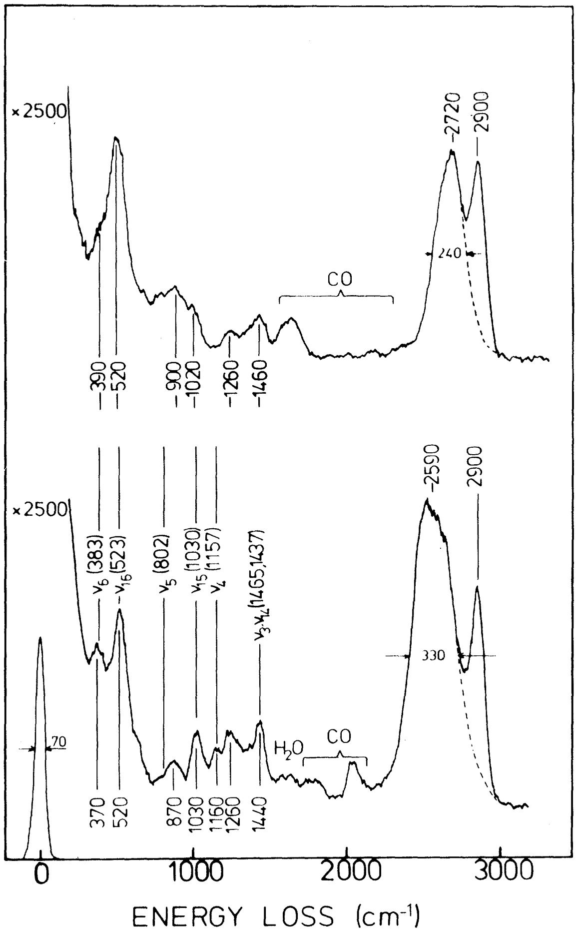

FIG. 1. Vibrational loss spectra for submonolayer adsorption of cyclohexane on Ni(111) (top) and on Pt(111) (bottom) at $T\sim 140$ K (5- and 2-Torr · sec exposures, respectively). The losses below 2000 cm^{-1} are assigned to the frequencies of the various a_{1g} and a_{2u} modes. [We also indicate between the two spectra these modes for the free molecule (Ref. 6).] The loss features of trace contaminants are indicated (coverage smaller than 0.02 of a monolayer).

Typical vibrational loss spectra for submonolayer adsorption of cyclohexane on both Ni(111) and Pt(111) surfaces for temperatures between 140 and 170 K are shown in Fig. 1. The same spectral features were obtained over a range of temperatures and coverages before multilayer condensation. We thus attribute this spectra to *one* adsorbed phase. This same phase of adsorbed cyclohexane has been studied on both Ni(111) and Pt(111) by uv photoemission[2,9] and shows valence ionization levels characteristic of cyclohexane which are distinct from those of other related cyclics (cyclohexene, cyclohexadiene, or benzene). With the exception of the unusually broad losses at 2720 and 2590 cm^{-1} on Ni and Pt, respectively, and the loss near 1260 cm^{-1}, the losses can be directly related to the a_{1g} and a_{2u} vibrational modes of gaseous cyclohexane.[6] Given the electron-loss surface selection rule that only modes with dipole moments normal to the surface can be excited,[10] these particular modes correspond to the ELS-active modes for a cyclohexane molecule oriented parallel to the surface. In this geometry, the 1260-cm^{-1} loss could be assigned to a corresponding set of perturbed CH_2 scission modes. If the molecule is not parallel to the surface but still has one symmetry plane perpendicular to the surface then the e_u modes would be ELS active in addition. The 1260-cm^{-1} loss in this case could then be assigned to the e_u CH_2 twisting mode. The $\left|\begin{smallmatrix}1 & 1\\ 4 & 5\end{smallmatrix}\right|$ LEED pattern which we observed on Ni(111) and which has been observed[11] on Pt(111) is consistent with a geometry where the molecule lies parallel to the surface or its slightly inclined to the surface. In either of these geometries three or one of the hydrogen atoms, respectively, would vibrate directly into the surface—a situation to which we can attribute the strong broadening and shifts of some of the CH vibrations.

On warming the sample, we find that cyclohexane reversibly desorbs from Ni for $T \gtrsim 170$ K but dehydrogenates on Pt for $T \gtrsim 200$ K to leave benzene. Both results are consistent with similar photoemission studies on Ni(111)[2] and Pt(111).[9] The unusual CH frequency softening and broadening is largest for the case in which the molecules undergo dehydrogenation at higher temperatures.

The unusual softening and broadening of some of the CH vibrational loss features is also observed for ethylene chemisorbed on Ni(111) but not for ethylene on Pt(111), as shown in Fig. 2. A discussion of the vibrational losses of ethylene on Pt(111) is given elsewhere[3] and at these (low) coverages is consistent with a chemisorbed molecule having C_{2v} symmetry. For all exposures of ethylene to Ni at $T \sim 140$ K, we find a single phase of chemisorbed ethylene which must have a lower point-group symmetry, C_s or C_1. Such a symmetry is deduced not only from the two groups of CH stretching vibrations but from the number of other losses observed, as well as from our studies of deuterated ethylene and the assignment of the observed vibrations. Such differences in symmetry suggest differences in the chemisorption bonding geometry which again may be associated with the occurrence of this CH vibration softening on Ni and not on Pt(111).

Upon warming the samples, we find that ethylene on Ni(111) converts to chemisorbed acetylene for $T \gtrsim 200$ K as found in photoemission studies,[2] but on Pt(111) converts to a different species, ethylidene (CH_3-$CH<$), for $T \gtrsim 280$ K.[3] Again, we observe softened CH vibrational losses only for the chemisorbed species that dehydrogenate at higher temperatures.

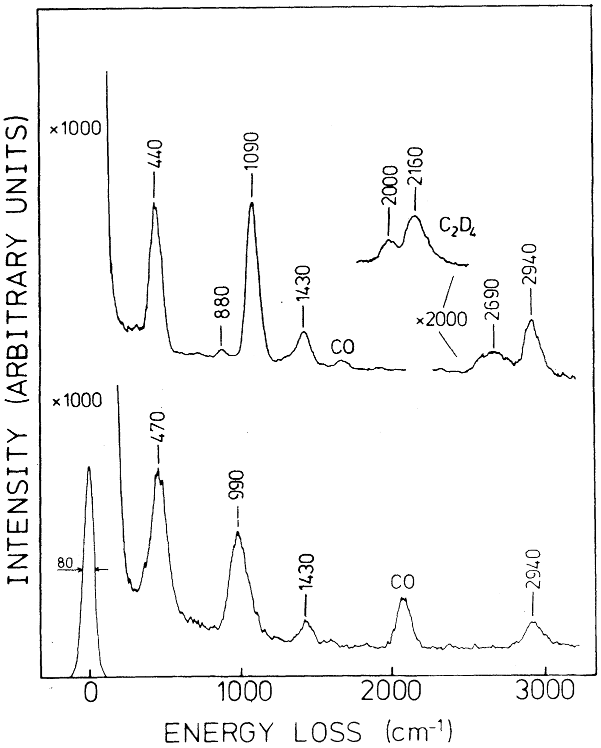

FIG. 2. Vibrational loss spectra for chemisorbed ethylene on Ni(111) (top) and on Pt(111) (bottom) for $T \sim 140$ K (3- and 1-Torr·sec exposures, respectively). The corresponding CD stretching region for the deuterated species on Ni shows broadening of both typical and atypical CD modes—a result which arises from the coupling of these two CD vibrations in the deuterated species.

The examples which we have presented show extra vibrational losses in the CH_n stretching region which have not been observed for other adsorbed hydrocarbons (C_2H_2 and C_6H_6) on Ni and Pt nor which have been observed in other infrared or Raman vibrational studies of adsorbed hydrocarbons or organometallic compounds.[6-8] As a result of the unusual nature of these losses one could argue that they may not reflect the true CH stretching vibration. To resolve this question, we have made additional measurements of of the angular dependence of these unusual loss features. As with any typical loss arising from an optical excitation, we find no dispersion in the width or frequency of this unusual loss arising from an optical excitation, we find no dispersion in the width or frequency of this unusual loss feature for cyclohexane for $q < 0.1$ Å^{-1}. Furthermore, the angular dependence of the intensity of this unusual loss feature agrees with other normal loss features (e.g., the CO stretching mode) and is well described by dielectric theory.[10] Thus, we correlate this unusual loss to the local CH potential and the forces experienced by the hydrogen atoms within the adsorbed molecule.

The spectral features we observe for these unusual CH stretching vibrations—the softening, broadening, and, for cyclohexane, the large integrated intensity—are characteristic of the spectral features observed for A-H stretching vibrations in hydrogen-bonded liquids.[12] For a molecule on a surface, we can associate the observed CH vibration softening and broadening to an attractive interaction between the surface atoms and certain hydrogen atoms of the molecule, similar to hydrogen bonding in liquids. An attractive interaction would also seek to bond some of the molecule's hydrogen atoms to the surface as supported by thermal desorption studies indicating the formation of chemisorbed hydrogen during dehydrogenation.[9] This additional attractive force on certain hydrogen atoms in the adsorbed molecule, along with the screening of the CH bond via the surface electron gas, can not only change the shape of the CH potential energy curve so as to lower the vibrational frequency, but can also reduce the activation energy needed to remove a hydrogen atom(s). This initial removal of a hydrogen atom(s) is believed to be the slow step in the dehydrogenation process, followed by more rapid conversion of partially dehydrogenated intermediates.[13] Whether quantiative information about reaction activation barriers can be obtained from changes in vibrational frequencies, as suggested by Anderson,[14] remains to be determined.

The broadening of the softened CH vibrational features cannot be attributed to a vibrational tunneling mechanism suggested in one case as the dehydrogenation reaction mechanism.[4] Such frequency broadening can arise from lifetime effects associated with electronic damping by the surface electron gas. Here, large substrate charge-density fluctuations may accompany CH vibrations which then decay by electron-hole excitations. Alternatively, as discussed for hydrogen bonding systems,[12] this broadening can be attributed to the strong coupling between these CH stretching vibrations and low-frequency molecule-surface vibrations. Clearly, further theoretical and experimental work is needed to fully understand the nature of this new electronic interaction, and its relation to hydrogen bonding.

We note that the inability to dehydrogenate cyclohexane on Ni(111) despite the observed CH vibration softening can be the result of a combination of the thermodynamic conditions used here (i.e., low pressures) and a higher activation barrier on Ni than on Pt. Namely, the temperatures needed to overcome the activation barrier on Ni may preclude the adsorbed species from remaining on the surface. However, our observation of CH vibration softening on Ni is consistent with the fact that dehydrogenation of cyclohexane does occur on Ni at higher pressures.[15] Thus, the study of vibrations may provide insight to reaction mechanisms or the presence of the interactions which drive the reaction *even for thermodynamic conditions under which the reaction may not occur*!

In summary, we observe unusual softening and broadening of some of the CH stretching vibrations of ethylene and cyclohexane adsorbed on Ni(111) and Pt(111) surfaces. This softening and and broadening appear to be directly related to dehydrogenation at higher temperatures, and can be attributed to an additional electronic interaction between some of the molecule's hydrogen atoms and the surface—possibly facilitated by the molecule's geometry on the surface. We postulate that this interaction reduces the activation barrier for CH bond scission so as to make dehydrogenation a preferred reaction path for these adsorbed species.

Finally, we note that the presence of such interactions on surfaces may also alter the vibrational frequencies of quasistable species or reaction intermediates which occur in synthesis or decomposition reactions. Although such frequency changes can introduce errors in deducing the chemical identity or nature of such species, these changes can also provide new and important information about surface reaction mechanisms.

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[1] R. P. Messmer, in *The Nature of the Surface Chemical Bond,* edited by G. Ertl and T. N. Rhodin (North-Holland, Amsterdam, 1978).

[2] J. E. Demuth and D. E. Eastman, Phys. Rev. Lett. 32, 1132 (1974), and Phys. Rev. B 4, 1523 (1976).

[3] H. Ibach, H. Hopster, and B. Sexton, Appl. Surf. Sci. 1, 1 (1977); H. Ibach and S. Lehwald, to be published.

[4] H. F. Winters, J. Chem. Phys. 62, 2454 (1975), and 64, 3495 (1976).

[5] C. N. Stewart and Gert Ehrlich, J. Chem. Phys. 62, 4672 (1975).

[6] Takehiko Shimanouchi, *Tables of Molecular Vibrational Frequencies, National Bureau of Standards Reference Data Series—39* (U. S. GPO, Washington, D. C., 1972), Vol. 1.

[7] L. H. Little, *Infrared Spectra of Adsorbed Species* (Academic, New York, 1966).

[8] E. Maslowsky, Jr., *Vibrational Spectra of Organometallic Compounds* (Wiley, New York, 1977).

[9] J. E. Demuth, unpublished results.

[10] E. Evans and D. L. Mills, Phys. Rev. B 5, 4126 (1972).

[11] L. E. Firment and G. A. Somorjai, J. Chem. Phys. 66, 2901 (1977).

[12] S. N. Vinogradov and R. H. Linnell, *Hydrogen Bonding* (Van Nostrand-Reinhold, New York, 1971), p. 52.

[13] D. W. Blakely and G. A. Somorjai, J. Catal. 42, 181 (1976).

[14] S. Anderson, Solid State Commun. 20, 229 (1976).

[15] G. C. Bond, *Catalysis by Metals* (Academic, London, 1962).