The Adsorption of Cyclopropane and Cyclohexane on Cu(111): An Experimental and Theoretical Investigation on the Nature of the CH–Metal Interaction**

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The nature of the interactions of molecules with surfaces is a topic of considerable importance in technology. For example, the chemical properties and dynamics of adsorbate systems directly underlie the reactivity patterns seen in heterogeneous catalysis.[1, 2] Related adsorption phenomena are also of relevance for many other areas, such as adhesion, wetting, lubrication, and corrosion inhibition.[3] For simple diatomic molecules such as CO bound to metal surfaces significant progress has been made in the past few years in moving from the early simple but valuable picture developed by Blyholder[4] to more recent, advanced descriptions.[5, 6] For the detailed understanding of interactions between hydrocarbons and metals, comparable approaches are just beginning to emerge. The adsorption of simple unsaturated hydrocarbons such as ethylene, acetylene, and benzene on Cu surfaces[7–10] are relatively well understood, and the early Dewar–Chatt–Duncanson model of these interactions[11, 12] has been improved significantly.

For saturated hydrocarbon adsorbates, the situation is less satisfying. In fact there are several properties of adsorbed alkanes on metals that are incompatible with the occurrence of simple physical interactions only. The most disturbing experimental observation is the now well-established occurrence of vibrational mode softening that results from metal–CH contacts, which was first reported by Demuth et al. 25 years ago for cyclohexane adsorbed on Ni(111) and Pt(111).[13] Similar observations have been reported since then for a variety of alkane adsorbates bound to many other substrates.[14, 15] A satisfying theoretical analysis of these unusual soft vibrational modes has been lacking—a surprising omission given the obvious relevance of such effects to the mechanisms of catalytic C–H bond activation. We have addressed this fundamental problem by a combined experimental and theoretical investigation of the binding of the small, highly symmetric saturated hydrocarbons cyclopropane and cyclohexane to Cu(111).

The reflection absorption infrared spectra (RAIRS) recorded for submonolayers of cyclopropane adsorbed on Cu(111) reveal only one C–H vibration at 3074 cm^{-1} (Figure 1, top). The observation of only one mode is expected

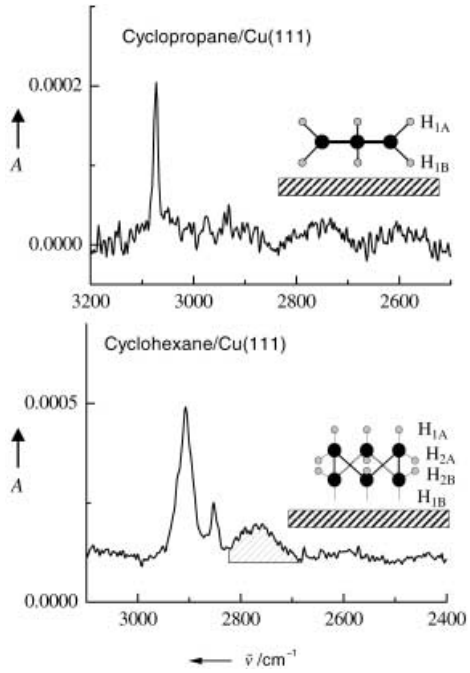

Figure 1. RAIR spectra recorded for a submonolayer of cyclopropane (top) and cyclohexane (bottom) adsorbed on Cu(111) at a surface temperature of 100 K. The two insets show the adsorption geometry for the two molecules. The hatched area shows the soft C–H stretch modes seen for adsorbed cyclohexane.

from the surface selection rule[16] applied to a planar cyclopropane adsorption geometry (Figure 1, insert). Soft modes in the frequency range between 2700 and 2900 cm^{-1}, which are commonly observed for saturated hydrocarbons adsorbed on copper surfaces, were not detected.[14, 17] Thus this is the first example for the adsorption of a saturated hydrocarbon on a Cu(111) surface, for which no soft modes occur.

The RAIR spectra for cyclohexane adsorbed on the Cu(111) surface (Figure 1, bottom) is very similar to that reported previously.[14, 17] In addition to the vibrations at 2907 and 2852 cm^{-1} expected for cyclohexane in a planar adsorption geometry with a chair conformation, pronounced soft modes, centered at 2770 cm^{-1}, with a half-width of 60 cm^{-1} and an integrated intensity of 50% of that of the dominant mode at 2907 cm^{-1} are clearly visible.

A comparison between the calculated ab initio frequencies provided in Table 1 and the experimental values strongly suggests that the soft modes seen for cyclohexane on the Cu(111) surface are in fact derived from the totally symmetric ν_2 mode (symmetric CH_2 stretch). That the adsorption-induced reduction of the molecular symmetry from D_{3h} to C_{3v} in principle makes the observation of this mode possible had been realized earlier.[14] No connection to the soft modes

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Table 1. Experimental and calculated frequencies for the free cyclohexane molecule (gp) and cyclohexane adsorbed in a planar geometry on a Cu(111) surface.

Mode[a]	Experimental			Calculated[b]		
	gp[c] [cm^{-1}]	Cu(111) [cm^{-1}]	Δ gp [cm^{-1}]	gp [cm^{-1}]	Cu(111) [cm^{-1}]	Δ gp [cm^{-1}]
ν_{25} EU CH_2 a-str	2933	–	–	3025 (123)	3010 (ia)[d]	15
ν_{26} EU CH_2 s-str	2863	–	–	2966 (37)	2959 (ia)[d]	7
ν_{12} a2u CH_2 a-str	2915	2907	8	3039 (156)	3024 (304)	15
ν_{13} a2u CH_2 s-str	2860	2852	8	2969 (87)	2959 (102)	10
ν_2 a1g CH_2 s-str	2852 (ia)	$\approx$2770	$\approx$80	2967 (ia)	2948 (50)	19

[a] The modes are labeled by the corresponding symmetry for the free molecule. Note that for the species adsorbed on the surface the symmetry will be lower. [b] The numbers in parentheses give the excitation probability; "ia" denotes IR-inactive. [c] Ref. [23]. [d] IR inactive because of surface selection rule (see text).

has yet been made, since the corresponding dynamic dipole moment, although finite, is expected to be very small for the ν_2 mode. This is nicely illustrated by the results of calculations for cyclopropane (Table 2), where the corresponding ν_1 mode is lower in intensity by about a factor of 40 with regard to the most intense vibration ν_6 of the adsorbed cyclopropane molecule. This small dynamic dipole moment explains why this mode is mot observed experimentally.

Inspection of the theoretical results for cyclohexane reveals, perhaps unexpectedly from an analogy made to the cyclopropane results, that the intensity of the symmetric CH_2-stretching ν_2 mode for adsorbed cyclohexane is of the same order of magnitude as that of the most intense ν_{12} mode (Table 1). This result suggests that for adsorbed cyclohexane a new mechanism comes into play. In fact a detailed analysis of the calculated data reveals that there is a significant transfer of charge from the Cu substrate into the adsorbed cyclohexane molecules.[18] Since this charge transfer depends very strongly on the distance of the molecule (in particular the proximal hydrogen atoms H_{1B}; Figure 1) from the surface, the dynamic dipole moment, $d\mu/dr$, for the cyclohexane ν_2 mode becomes significant and, accordingly, makes the ν_2 mode very intense. The strongly distance-dependent charge transfer thus provides a well-supported explanation as to why the ν_2 mode is so intense for the adsorbed cyclohexane molecule. Although the calculated frequency shift relative to the gas-phase, $-19\,cm^{-1}$, is by far the largest seen for any of the cyclohexane modes characterized here, the absolute shift does not agree in a quantitative way with that seen in the experiment ($\approx -80\,cm^{-1}$). This latter discrepancy most likely results from systematic errors associated with the finite size of the Cu cluster used and is expected to decrease in magnitude with an increasing cluster size.

From a chemical point of view, the occurrence of significant (and specific forms) of charge transfer is very important for understanding the reactivity of hydrocarbons adsorbed on metal surfaces and is of relevance for developing an understanding of the relationship between structure and rate of reaction in C–H bond activation processes on solid surfaces. The results of the theoretical analysis for the different contributions to the interactions occurring between the adsorbate and substrate[18] suggest that a heretofore unappreciated mechanism exists that leads to a charge transfer into empty molecular orbitals with predominantly Rydberg character. Such a transfer can be considered a form of back-donation, since it is one that passes from the substrate into the molecule. We note that this charge transfer bears no similarity to a Blyholder donation/back-donation model such as might describe the binding of CO on metal surfaces[4–6] or a Dewar–Chatt–Duncanson type donation/back-donation scheme[11, 12] that defines aspects of the interactions of unsaturated hydrocarbons with metal substrates.

The driving force for the charge transfer into the cyclohexane molecule is the dispersion forces pulling the hydrocarbon towards the metal states. This attraction is eventually compensated by the Pauli repulsion between the HOMOs of the cyclohexane and the metal states. If the attraction is sufficiently strong, as appears to be the case for cyclohexane, some degree of the metal charge will flow into the molecule. This charge flow dominates the perturbations of the spectroscopy noted above. That the charge is back-donated into Rydberg orbitals and not into orbitals of C–C σ^* or C–H σ^* character also explains why the changes in the adsorbate intramolecular geometry are at best only minor. For the case of a back-donation into, for example, CH σ^* orbitals one would expect a significant increase of the C–H bond length.

Calculations should help to explain why the charge transfer is so much smaller for cyclopropane than for cyclohexane. As noted above, a detailed investigation revealed a strong dependence of the extent of charge transfer on the distance between the surface and molecule. The optimized adsorption geometry for cyclohexane yields a distance of 2.75 Å between

Table 2. Experimental and calculated frequencies for the free cyclopropane molecule (gp) and cyclopropane adsorbed in a planar geometry on a Cu(111) surface.

Mode[a]	Experimental			Calculated[b]		
	gp[c] [cm^{-1}]	Cu(111) [cm^{-1}]	Δ(gp) [cm^{-1}]	gp [cm^{-1}]	Cu(111) [cm^{-1}]	Δ(gp) [cm^{-1}]
ν_6 A_2'' CH_2 as-str	3103	3074	29	3238 (41)	3218 (69)	20
ν_8 E′ CH_2 s-str	3038	–	–	3120 (21)	3101 (ia)[d]	19
ν_1 A_1 CH_2 s-str	3025 (ia)	–	–	3136 (ia)	3110 (1.2)	26

[a] The modes are labeled by the corresponding symmetry for the free molecule. Note that for the species adsorbed on the surface the symmetry will be lower. [b] The numbers in parentheses give the excitation probability; "ia" denotes IR inactive. See text for details on calculations. [c] Ref. [23]. [d] IR inactive because of surface selection rule (see text).

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the H_{1B} atoms and the Cu surface. The corresponding distance between the H_{1B} atoms of cyclopropane and the surface is 3.0 Å. It thus appears that the dispersion forces for cyclopropane are not quite strong enough to push the molecule as deeply into the surface, which results in a lesser degree of charge transfer into the molecule than occurs for cyclohexane.

Experimental Section

The UHV chamber used in these experiments was operated at a base pressure of $< 3.0 \times 10^{-10}$ Torr and has been described previously.[19, 20] The RAIRS data were collected with a Digilab FTS 60A spectrometer with a liquid nitrogen cooled wide-band MCT detector in conjunction with external reflection optics, maximized for single grazing angle reflection. The crystal temperature was monitored by a chromel-alumel thermocouple lodged in a hole on the side of the crystal. The crystal could be cooled and heated within the temperature range of 100 – 950 K. The crystal was cleaned by sputtering with 1 keV Ar^+ ions for 30 min at 850 K and then annealed for 15 min at 850 K. The adsorbates were introduced into the chamber by using an effusive molecular beam doser located approximately 5 cm from the crystal. Cyclopropane (> 99 %) was obtained from Aldrich and used as received. Cyclohexane (> 99 %) was obtained from EM Science and degassed by freeze-pump-thaw cycles before introduction into the chamber. The pressure during dosing varied between 1×10^{-9} and 5×10^{-7} Torr. Exposures, reported in Langmuirs (1×10^{-6} Torr), are not corrected for the ion gauge sensitivity.

Ab initio calculations: The calculations for cyclopropane and cyclohexane adsorbed on Cu(111) closely follow an approach described previously.[21] Briefly, high-quality ab initio Hartree – Fock calculations were carried out for a (7,3)-cluster exhibiting C_{3v} symmetry modeling a Cu(111) surface with a Cu lattice constant of 2.54 Å using a commercial software package (Gaussian 98[22]). Correlation effects were included at the MP2 level. For the Cu atoms a 28-electron pseudopotential (see reference [21] and [23] for a detailed discussion) together with an extensive basis set for the remaining electrons was used together with a 6-311 ++ basis set for the C and the H atoms. This basis set has been demonstrated to be sufficiently large to account for the details of the alkane electronic structure seen in X-ray absorption spectroscopy[24] and to the corresponding adsorption-induced changes in those data.[21] Previous work has shown that this theoretical approach provides a very reasonable potential for the cyclopropane/Cu(111) interaction, giving good agreement with experimental quantities such as the binding energy and the curvature of the surface – molecule potential.[21] All results reported here were obtained for the electronic ground state of the Cu(7,3)-cluster, which is a triplet state.

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Pentaphosphaferrocene as a Linking Unit for the Formation of One- and Two-Dimensional Polymers**

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Dedicated to Professor Joachim Strähle on occasion of his 65th birthday

Common approaches in the field of self-organization of discrete supramolecular[1] aggregates, networks, and coordination polymers[2] make use of N-donor containing ligands and N-heterocycles to connect different metal centers together. In contrast, however, our goal in this field has been the use of P_n-ligand complexes as linking moieties between metal cations to form well-oriented assemblies as well as one-dimensional (1D) and two-dimensional (2D) polymers.

The coordination chemistry of P_n-ligand complexes[3] towards cationic metal centers (excluding cationic organometallic complex moieties[4]) has so far been limited to the use of *cyclo*-P_3-ligand complexes, such as [(triphos)M(η^3-P_3)] (M = Co, Rh, or Ir; triphos = 1,1,1-tris(diphenylphosphanylmethyl)ethane), which usually form metal-bridged dimers.[5]

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