

# Spin uncoupling in surface chemisorption of unsaturated hydrocarbons

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Unsaturated hydrocarbons, such as acetylene and ethylene, show strong geometrical distortions when coordinated to transition metals or to surfaces; the bonding is normally analysed in terms of a  $\pi$ -donation— $\pi^*$ -backdonation process. In the present work we use chemisorption of the unsaturated hydrocarbons (ethylene, acetylene, and benzene) on cluster models of the copper (100), (110), and (111) surfaces to demonstrate the importance of considering the available excited states of the free molecule in analyzing the bonding scheme of the adsorbate at the surface. By comparison to the structures of the triplet excited states in the gas phase we demonstrate that these must be considered as the states actually involved in the bonding. This implies a spin-uncoupling in both adsorbate and substrate as part of the chemisorption process or bond formation. In particular, for benzene we identify the quinoid gas phase triplet state as the specific state that is most strongly bound to the Cu(110) substrate; the structure is an inverted boat form. The gas phase antiquinoid triplet state leads to a planar, less strongly bound, chemisorbed state. By explicitly considering the excited state of the adsorbate that corresponds to the bonding state—the ground state for the chemisorbed system—barriers in the chemisorption path are analyzed in terms of avoided crossings between the initial closed-shell singlet state and the bond-prepared excited triplet state, which, together with the substrate, forms an overall singlet. It is argued that this picture with bond-preparation through spin-uncoupling can be very useful to understand and predict reaction paths in heterogeneous catalysis. © 1998 American Institute of Physics. [S0021-9606(98)00203-7]

## I. INTRODUCTION

The interaction of unsaturated hydrocarbons with metal surfaces has great implications for surface chemistry and catalysis and has consequently attracted substantial attention over the years. Recently, with the availability of refined experimental and theoretical techniques, there has been a resurgence of the interest and new attempts to elucidate the detailed binding mechanisms of e.g., acetylene, ethylene, and benzene to different metal substrates. Both acetylene and ethylene, are, for many of the surfaces, found to undergo substantial C–C bond elongations indicative of a strong rehybridization. In addition, the  $\sigma$ – $\pi$  separation as seen in near-edge x-ray absorption spectroscopy (NEXAFS) or x-ray emission spectroscopy (XES) is to some extent lost for the adsorbed species. This is normally interpreted as an effect of the rehybridization or repulsion against the surface resulting in a bending up of the hydrogens from the surface. These large geometrical distortions are, in seeming contradiction, combined with a rather low chemisorption energy.

Unsaturated hydrocarbons on metallic surfaces are of considerable interest from the experimental and theoretical points of view because they form important models for catalytic processes in general and because they represent several key aspects which motivate studies by theoretical simulations. The study of organometallic compounds dates from 1827 when Zeise<sup>1</sup> heated a  $\text{PtCl}_2 + \text{PtCl}_4$  mixture in ethanol, evaporated the solvent and treated the residue with aqueous KCl. The product was Zeise's salt  $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ , the nature of which was not understood until x-ray studies in the

early 1950s showed that the ethylene molecule was coordinated approximately perpendicular to the molecular plane of the anion, with the hydrogens bent away from the metal. A molecular frontier orbital approach to the bonding in this complex, first developed by Dewar, Chatt, and Duncanson,<sup>2,3</sup> serves as a paradigm for bonding in  $\pi$ -complexes. In this model the  $\pi$ -system donates charge into unoccupied levels of the metal while the  $\pi^*$ -level becomes occupied through back-donation. The resulting loss of bonding character in the  $\pi$ -level and increased antibonding character through occupation of the  $\pi^*$  orbital leads to a loss of bond-order and thus an increased C–C bond distance.

The C–C bond elongation is accompanied by a bending of the hydrogens away from the surface or from the metal center, which normally is interpreted in terms of a repulsion effect. However, this type of structure is nearly identical to what is found for the gas phase excited triplet states of these molecules, where the  $\pi$ – $\pi^*$  triplet excitation also leads to a substantial bond elongation and, in addition, a bending of the hydrogens. In fact, since the excitation corresponds to a rehybridization of the carbons, triplet-excited acetylene assumes a structure close to that of ethylene (with two hydrogens removed) and triplet-excited ethylene resembles ethane; again with two hydrogens removed and with the possibility to assume eclipsed and staggered (twisted) conformations. Noting the structural similarity between these gas phase excited states and those of the chemisorbed or interacting molecules, it is very tempting to propose the explicit involvement of the triplet-excited state in the chemisorption process.

The similarity between the structures obtained for acetylene and ethylene on Pt(111) and Ni(111) and those of the respective gas phase excited triplet states was early pointed out by Felner and Weinberg.<sup>4</sup> They compared the vibrational frequencies for the adsorbed systems with those of the triplet states and found a very good correspondence. A similar analysis was performed by Freund and co-workers in their study of the  $\alpha$ -state of  $N_2$  on Fe(111);<sup>5</sup> in this geometry the molecule is found to lie down on the surface with an internal geometry that is best understood in terms of the  $A^3\Sigma_u^+$  excited state. It is noteworthy that the gas phase excitation energy to reach this state is very high, over 140 kcal/mol, but still this state was identified as involved in the formation of the lowest-energy bonding state at the surface. Later Carter<sup>6</sup> and Carter and Koel<sup>7</sup> presented a thermochemistry scheme for calculating the heats of formation of adsorbed species on metal surfaces using two pieces of gas phase data; (i) the heat of formation for the gaseous species in their ground electronic state; (ii) the electronic excitation energy necessary to put the molecule into the appropriate bonding state. This, combined with typical metal ligand bond strengths and experimental estimates of rate determining activation energies, enabled a thorough analysis of the intermediate steps in the decomposition of ethylene on Pt(111). Rochefort *et al.*<sup>8</sup> considered also the excited states to generate starting structures in an investigation of the interaction of *c*- $CH_2N_2$  on Pd(110) and Cu(110), but for the most part there seems not to have been any consistent application of these ideas. Recently Hermann and co-workers have investigated the interaction of both acetylene and ethylene with the Cu(111) surface<sup>9,10</sup> and pointed out the large energy cost associated with the deformation of the molecule into the structure found at the surface. As a consequence of this, they concluded that the measured low chemisorption energy could not be used to draw conclusions about the strength of the interaction; considering the large changes in the geometries upon adsorption, the low chemisorption energy must rather be seen as the resulting balance of a rehybridization cost and the gain from the formation of bonds to the surface. A similar conclusion was reached by Clotet and Pacchioni<sup>11</sup> in their comparison of  $C_2H_2$  chemisorption on Cu(111) and Pd(111); on copper the adsorption was concluded to be an activated process, while adsorption on palladium was found to occur without a barrier. Performing a constrained space orbital variation analysis (CSOV) (Refs. 12, 13) at different points of the interaction curve they could show that the main difference between the two metals referred to the occupation of the *sp* band on copper which leads to higher repulsion effects, but also larger backdonation mainly involving *sp* electrons. The smaller amount of back-donation in the interaction with the Pd substrate was found to lead to smaller values for the C–C bond elongation and vibrational frequency shifts in agreement with experiment.

In the present work we focus on the role of precursor electronic and geometric structures of the reactants in order to obtain a proper preparation for the surface adsorption. Based on numerical results for optimum geometries, excitation, and bonding energies, we argue that the surface adsorp-

tion implies an explicit spin uncoupling in the adsorbate which exactly corresponds to the excitation to its triplet state. Two triplet states emerge during the adsorption process; a triplet adsorbate state and a local triplet surface state, and these are coupled to produce the total singlet state spin-pairing typical for two localized metal-to-carbon bonds. This implies that the adsorbate geometry should be prepared for the high-spin state in the simulation of the adsorption. In the case of unsaturated hydrocarbons these prepared states have a higher dimensionality than in the gas phase; acetylene goes from linear to planar, ethylene from planar to three-dimensional and benzene can assume an inverted boat conformation on Cu(110). Thus, the  $\sigma$ – $\pi$  separability is broken, as indeed is observed from NEXAFS and XES studies. Furthermore, we find a remarkably stable Cu–C individual bond energy with an average of  $50 \pm 3$  kcal/mol for acetylene and ethylene on Cu(100), Cu(110), and Cu(111). For benzene a larger, 58 kcal/mol, individual bond strength on Cu(110) is obtained. Thus, we reinterpret the computed barriers found in the interaction curves for acetylene<sup>11</sup> and ethylene<sup>10</sup> on Cu(111) to correspond exactly to the simultaneous excitation of the adsorbate and substrate into two internally triplet spin-coupled entities which, through this process, become prepared for bonding. The total spin is always the low-spin state found at large distances so no overall change of the spin is implied.

It should be noted that bond-preparation as a concept has earlier mainly been applied to the cluster to improve the results in comparison with the extended surface.<sup>14</sup> In this context it relies on a careful, a posteriori, analysis of the electronic state of the cluster in the wave function describing the ground state of the cluster plus adsorbate; the same cluster electronic state should then be used when computing the energy for the separated system. Spurious effects of the discreteness of the levels due to the use of a cluster model are thus eliminated or reduced. In the present case we apply this concept to both the adsorbate and the substrate, but for two different purposes; for the adsorbate, which naturally has a discrete level structure we will use it to determine the actual excitation energy required to prepare the adsorbate for bonding. This can be applied both a priori if it is known what types of bonds a particular adsorbate should form, or a posteriori as an analysis of which excited state of the gas phase adsorbate the ground state for the chemisorbed system corresponds to. Both substrate and adsorbate naturally need to be prepared for bonding, but for the extended metal substrate, with a continuous density of states around the Fermi level, we will assume that the energy cost is negligible and use the normal cluster bond-preparation technique in the traditional sense; to correct, when necessary, for the discreteness of the levels in the cluster. Note that when the interaction to be analyzed involves a true cluster, a transition metal atom or a single molecule, the discreteness of the levels is real and must be explicitly considered.

The organization of the paper goes as follows. In the next section we describe the details of the calculations followed by separate discussions of the results for properties of the three different systems studied. Acetylene chemisorption

on Cu(100), Cu(110), and Cu(111) is discussed in Sec. III A, ethylene in Sec. III B, and finally the case of benzene on Cu(110) and Cu(100) is discussed in Sec. III C. In Sec. IV the overall trends and general conclusions are presented.

## II. COMPUTATIONAL DETAILS

The present study uses a series of copper clusters to model the interaction of the acetylene, ethylene, and benzene molecules on the different low-index copper surfaces [(100), (110) and (111)]. For the acetylene and ethylene molecules we have studied the di- $\sigma$  adsorption site for all surfaces, while for the (111) surface we have also included the cross-bridge site and (for acetylene) the hollow fcc- $h_{\parallel}$  site which is found to be the most stable by Clotet and Pacchioni.<sup>11</sup> In the di- $\sigma$  orientation, both the acetylene and ethylene molecules are placed with the C–C axis parallel to the nearest Cu–Cu neighbor pair on the substrate surface. In the second orientation, namely cross-bridge, the adsorbates ( $C_2H_2$  and  $C_2H_4$ ) are also placed with the C–C axis parallel to the surface at the  $C_s$  mirror plane of the substrate cluster, but with the carbons pointing towards adjacent fcc and hcp hollow sites. The (110) and (100) surfaces were modelled by a cluster of 14 atoms [Cu(8,6)] with 8 atoms in the first layer and 6 in the second, while the (111) surface was described by a Cu(4,3) or Cu(12,6,1) cluster of  $C_s$  symmetry. All structures were fully gradient-optimized on each cluster model using the deMon density functional (DFT) program<sup>15,16</sup> with the gradient corrected BP86 exchange and correlation potentials. The cluster was always kept fixed at the bulk bond distance 2.556 Å.<sup>17</sup> All metal atoms were treated at the all-electron level.

For benzene the structure was optimized on two different, all-electron Cu<sub>13</sub> clusters modeling the Cu(100) and the Cu(110) surfaces, respectively. Several different starting geometries were investigated;  $C_{2v}$  symmetry constraints were maintained in order to reduce the size of the calculations.

In the present work the chemisorbed states will be compared to the explicitly excited triplet states of the gas phase systems; this excitation corresponds exactly to the bond-prepared adsorbate states for all three adsorbates. For this comparison we have optimized the gas phase geometries of the acetylene, ethylene and benzene molecules both in their ground ( $^1A_g$ ) and in their triplet ( $^3B_u$ ) states, and analyzed different conformations in their respective triplet state, namely *cis* and *trans* for acetylene, eclipsed and staggered for ethylene, and quinoid and antiquinoid for benzene; in all cases we have computed the adiabatic singlet–triplet splitting ( $\Delta$ ) and compared with the corresponding value for the triplet in the structure obtained from the cluster calculations. For the gas phase calculations the GAUSSIAN94 (Ref. 18) program was used for the DFT calculations with the B3LYP (Ref. 19) functional to describe exchange and correlation. The 6-311G(*d*) (Refs. 20, 21) basis set was used in these calculations.

The deMon program reduces the four-center Coulomb integrals to three-center ones by fitting the Coulomb interaction to an auxiliary basis set. Similarly, the exchange-correlation potentials and energies are interpolated on the

numerical grid using a second auxiliary basis set; this allows a coarser grid to be used until convergence is reached, at which point the grid is tightened and an accurate numerical quadrature is performed. The auxiliary basis used for hydrogen in the DFT calculations was (3,1;3,1) (Ref. 22) consisting of 3/1 exponents for the inner/outer parts of the Coulomb potential and of  $V_{xc}$ , respectively. The inner part uses only *s*-type functions, while for the outer part *s*, *p*, and *d*-functions having the same exponents are generated. For copper the original (5,5;5,5) basis by Godbout *et al.*<sup>22</sup> is used, while for carbon the auxiliary basis was (5,2;5,2). The all-electron orbital basis set for Cu was that of Wachters<sup>23</sup> using an [8*s*,5*p*,3*d*] contraction with one diffuse *p* function and one *d* function added. For hydrogen the primitive (5*s*) basis set from Ref. 24 was used, augmented with one *p* function and contracted to [3*s*,1*p*], while for carbon triple-zeta valence polarization (TZVP) (Ref. 25) was used in a generalized [4*s*,3*p*] contraction and with one added *d* function. These basis sets were used both for the optimization of the geometries and for the determination of the chemisorption energies.

In employing a cluster model to determine chemisorption energies for the extended surface, care must be taken to avoid artificial oscillations with cluster size.<sup>14</sup> Thus, the chemisorption energy should in general not be computed with respect to the lowest state of the naked cluster, but rather with reference to the electronic state of the cluster that is most similar to that actually involved in the bonding. In order to bond to the adsorbate, i.e., to reach the lowest energy state for the chemisorbed system, the cluster may have to be excited to the bonding state. This excitation should be a negligible energy cost when it occurs around the Fermi level of the extended surface, but may be sizable for a limited cluster. This effect may be compensated by performing the excitation also at long distance for the naked cluster. This is of special importance in the present case where the adsorbate molecules form local bonds to the substrate requiring two open shells of the appropriate symmetries on the cluster (and on the adsorbate). For Cu(110) and Cu(100) the clusters are already prepared for bonding, i.e., the cluster ground state is the required triplet state, but for Cu(111) the seven-atom Cu(4,3) cluster has an excitation energy of 30 kcal/mol as cluster correction. This is too large to allow a reliable prediction of a chemisorption energy and thus the chemisorption energy was computed for a larger 19-atom Cu(12,6,1) all-electron cluster. For the latter the cluster correction amounts to 9 kcal/mol which is sufficiently small to allow it to be used to calculate the chemisorption energy.

Note that no excited states are considered for the chemisorbed system; even though the analysis shows that the adsorbate is best described as correlating to the excited triplet state it is still the lowest electronic state for the cluster with adsorbate for that particular geometry. Similarly, we may find that the electronic state of the cluster in the combined system is best described as related to an excited state of the naked cluster; this is then used as reference to put the cluster excitation energy to zero (or approximately zero) as is appropriate for the extended system that the cluster is designed

TABLE I. Optimized geometries ( $\text{\AA}$ ) and adiabatic singlet-triplet excitation energies ( $\Delta$ , kcal/mol) for acetylene in the gas phase optimal geometries and for the gas phase species in the surface-optimized geometries. The chemisorption energies  $D_e$  (kcal/mol) are computed with respect to the bond-prepared cluster at large distance (with respect to lowest cluster state in parentheses).

Property	Gas phase		Adsorbed				
	Singlet	Triplet	(110) di- $\sigma$	(111) CB <sup>a</sup>	(111) di- $\sigma$	(111) fcc- <i>h</i>	(100) di- $\sigma$
C–C	1.20 (1.208) <sup>b</sup>	1.32 (1.325) <sup>c</sup>	1.31	1.40	1.34	1.37	1.30
C–H	1.06 (1.06) <sup>b</sup>	1.09 (1.084) <sup>c</sup>		1.09	1.10	1.10	1.09
C–C–H	0.0	128.3 (128.1) <sup>c</sup>	131.1	125.7	125.5	123.6	134.3
$\Delta$	0	85 (88) <sup>c</sup>	86	89	86	87	87
$D_e$	...	...	15	13(4) <sup>d</sup>	15(6) <sup>d</sup>	16(7) <sup>d</sup>	20

<sup>a</sup>Cross-bridge adsorption site.

<sup>b</sup>Experimental data from Ref. 48.

<sup>c</sup>CCSD(T) results from Ref. 26.

<sup>d</sup>Cu<sub>19</sub> cluster with doublet–quartet excitation energy 9 kcal/mol used; see text.

to model. Thus, at short distance we only consider the lowest electronic state of the cluster with adsorbate; at long distance we consider the states that correlate with the chemisorbed state.

### III. RESULTS

We have optimized the structures of the three adsorbates, acetylene, ethylene, and benzene, by means of density functional theory (DFT) in its generalized gradient approximation using cluster models of the three low-index copper surfaces; Cu(100), Cu(110), and Cu(111). Except for the di- $\sigma$  state of ethylene on Cu(111) and for benzene on Cu(100) we find in all cases large distortions of the internal adsorbate structures; the C–C bond distance in the adsorbate is strongly elongated and the hydrogens are found to bend away from the surface. In the case of benzene on Cu(110) we find two structures, where the more strongly bound has the planar ring structure distorted into an inverted boat structure with C–C distances in good correspondence with the quinoid form of the excited triplet state of gas phase benzene.

In this section we will present our results for structures of the chemisorbed unsaturated hydrocarbons and compare these with the corresponding triplet-excited gas phase structures and with experimental or earlier theoretical data. We focus on results for the adiabatic excitation between the singlet and triplet states, each in its optimum gas phase structure, or to the gas phase triplet state artificially in its optimum chemisorbed structure. The latter excitation energy gives explicitly the rehybridization cost and, by comparing with the adiabatic excitation energy, one obtains a measure of the sensitivity of the triplet-state potential energy surface to changes in the bond length. The latter is of importance in predicting chemisorption properties on different substrates with different metal–metal distances.

#### A. Acetylene

The first excited triplet state of acetylene corresponds to a  $\pi \rightarrow \pi^*$  excitation, leading to a loss of bond order and a substantial (0.12  $\text{\AA}$ ) elongation of the bond (Table I and Fig. 1). The resulting bond length is very similar to that found for

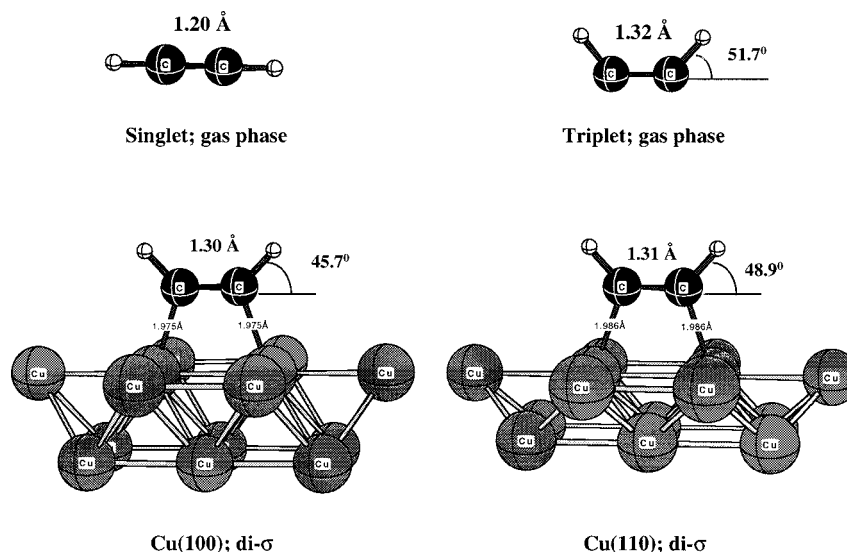


FIG. 1. C<sub>2</sub>H<sub>2</sub> gas phase (singlet and triplet) with C<sub>2</sub>H<sub>2</sub>/Cu(110) and C<sub>2</sub>H<sub>2</sub>/Cu(100).

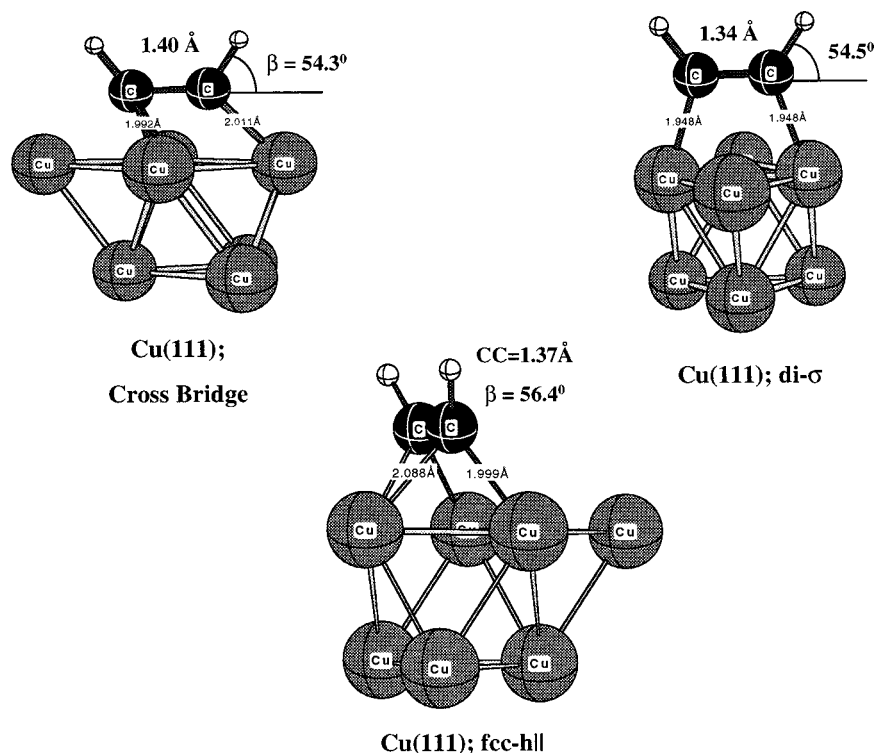


FIG. 2.  $C_2H_2$  on Cu(111); cross bridge, di- $\sigma$  and fcc- $hll$  adsorption sites.

ethylene and the hydrogens are found to bend up giving a C–C–H angle that is close to  $130^\circ$ , as in ethylene. The excitation to the triplet state thus corresponds to a rehybridization going to  $sp^2$ -hybridized carbons with a radical character; each of the carbons may now be considered to be prepared for forming a covalent bond to the substrate by means of the unpaired electron in the former  $\pi$  and  $\pi^*$  orbitals.

In the case of chemisorbed acetylene the variations in bond-length are between 0.11–0.20 Å with the longer C–C bond corresponding to the adsorption on the (111) surface in the cross-bridge site. The second important parameter is the C–C–H angle; for the adsorbed species the obtained angles vary between  $126^\circ$  on the (111) surface to  $134^\circ$  on the (100) surface, see Figs. 1 and 2. A crucial point in the present investigation is to examine the correlation between the geometry of the adsorbed molecule and the geometry of the excited triplet state of the free molecule. [There are two forms of triplet acetylene close in energy; the *trans* ( $^3A_u$ ) and the *cis* ( $^3B_2$ ) forms. Only the *cis*-form ( $C_{2v}$  symmetry) is important in the context of interaction with the surface; the *trans*-form is computed to be some 10 kcal/mol higher in energy and can furthermore not form the required two bonds to the surface. See also Ref. 26.] Comparing the obtained geometrical parameters with those of the excited triplet state, the similarities are very evident for all three substrates.

Hermann and Witko<sup>9</sup> and Clotet and Pacchioni<sup>11</sup> have discussed the energy cost to reach the geometrically distorted structure of the chemisorbed acetylene. The comparison has, however, in both cases been with the distorted closed-shell singlet state which we argue is not the state involved in

bonding. It is clear from previous work<sup>5–7</sup> as well as from the present study that the excitation energy to reach the bond-prepared state of the adsorbate is substantial; considering the binding state to be the triplet-excited molecule we find a computed adiabatic excitation energy of 85 kcal/mol in the gas phase, which can be compared to the early CI-value of 80.4 kcal/mol of Wetmore and Schaefer<sup>27</sup> and the later, more accurate study using CCSD(T) combined with large basis sets which gave a value for the adiabatic excitation energy of 88 kcal/mol.<sup>26</sup> Experimentally it seems difficult to determine an accurate value for this excitation energy, both due to the spin-forbiddenness using optical spectroscopies and due to the low Franck–Condon overlap for the lowest vibrational states from the large structural change upon excitation.<sup>28</sup> An upper bound of 4.62 eV (106 kcal/mol) for the  $^3B_2$  excitation was given,<sup>28</sup> but it seems likely that the high-level theoretical value (88 kcal/mol) of Ref. 26 should give a more accurate estimate. However, it is clear that the present simple DFT result is quite within the range of results from more advanced theoretical techniques.

Only considering the lowest singlet state at different geometries on the way to the chemisorbed structure Clotet and Pacchioni<sup>11</sup> find an activation energy of 64 kcal/mol at the MP2 level, while Hermann and Witko<sup>9</sup> find 55 kcal/mol at the CI-level and 90 kcal/mol from the Hartree-Fock calculation; it is clear that dynamical correlation plays an important role in reducing the cost to distort the molecule. Hermann and Witko explicitly considered the intersection between the singlet ground state and the excited triplet state as a measure of the energy barrier to reach the distorted geometry. In the latter case an activation energy of about 70 kcal/mol is re-

TABLE II. Optimized geometries ( $\text{\AA}$ ) and adiabatic singlet-triplet excitation energies ( $\Delta$ , kcal/mol) for ethylene in the gas phase optimal geometries and for the gas phase species in the surface-optimized geometries. The chemisorption energies  $D_e$  (kcal/mol) are computed with respect to the bond-prepared cluster at large distance (with respect to lowest cluster state in parentheses).

Property	Gas phase				Adsorbed			
	Singlet	Triplet Eclipsed staggered		(110) di- $\sigma$	(111) CB <sup>a</sup>	(111) di- $\sigma$	(100) di- $\sigma$	
C–C	1.33 (1.337) <sup>b</sup>	1.54	1.45	1.39	1.51	1.35	1.46	
C–H	1.09 (1.08) <sup>b</sup>	1.08	1.09	1.09	1.09	1.09	1.09	
C–C–H	121.7	118.7	121.9	119.2	114.1	121.3	116.2	
$\Delta$	0	83	64	92	87	... <sup>c</sup>	86	
$D_e$	...	...	...	13	$-16(-25)$ <sup>d</sup>	5	6	

<sup>a</sup>Cross-bridge adsorption site.

<sup>b</sup>Experimental data from Ref. 48.

<sup>c</sup>Undistorted physisorbed state.

<sup>d</sup>Cu<sub>19</sub> cluster with doublet–quartet excitation energy 9 kcal/mol used; see text.

ported at the self-consistent field (SCF)-level, with an estimated reduction from dynamical correlation down to 20–30 kcal/mol. This latter value is quite low compared both with our present results and those of Clotet and Pacchioni.

It is interesting to compare the results for chemisorption on the different surfaces where, for the di- $\sigma$  chemisorption geometry, the resulting optimized C–C bond distance is always close to that of the triplet state with only small variations. The corresponding excitation energies are thus also rather similar to the gas phase acetylene and vary only by a few kcal/mol for the different geometries. For the cross-bridge chemisorbed state on a Cu(111) surface the increase in bond-length is much larger, 0.20  $\text{\AA}$ , but this still leads to only a small, 4 kcal/mol, increase in the required excitation energy over the computed adiabatic gas phase value.

To draw conclusions about the possible mechanism for the adsorption of the hydrocarbon molecules, we have in addition to the geometric analysis in terms of bond distance and angle variations, performed an energy analysis in terms of separate energy costs of rehybridization of the carbons upon adsorption and energy gain from formation of new surface bonds. Such an analysis is in the spirit of the study of Hermann and Witko on the interaction of acetylene on the Cu(111) surface,<sup>9</sup> in which it was pointed out that the overall weak C<sub>2</sub>H<sub>2</sub>–Cu(111) interaction is determined by a competition between the energy required to change the geometry in the adsorbed molecule and the energy gained due to local bond formation of the distorted molecule. In Table I we give the computed chemisorption energies for the different surfaces studied within the cluster model approach. Here it should be noted that for the small Cu(4,3) cluster representing the Cu(111) surface the ground state is a doublet state and the excitation to reach the bond-prepared quartet state of the cluster is 30 kcal/mol. This is too much for this type of correction to be applicable<sup>14</sup> and the Cu(4,3) cluster is thus not suitable for use in predicting chemisorption energies; a cluster with lower-lying excitations, more like the extended surface, must thus be found. For the Cu<sub>19</sub>(12,6,1) cluster the doublet–quartet excitation energy is 9 kcal/mol, which makes it more suitable for computing the chemisorption energy; this

cluster was thus used to obtain the values for the Cu(111) cluster in the table. Note, however, that for accurate predictions of chemisorption energies from cluster models of a substrate, several clusters with different size should be used and the average of the computed chemisorption energies used as the predicted value.<sup>14</sup>

We define the interaction energy ( $E^{\text{int}}$ ) as the sum of  $\Delta$ , the adiabatic singlet–triplet excitation energy required for the rehybridization of the active carbon atoms, and the chemisorption energy,  $D_e$ .  $\Delta$  is calculated without the substrate as  $\Delta = {}^3E_1 - {}^1E_0$ , where  ${}^3E_1$  is the first excited triplet state energy calculated in the gas phase using the optimized geometry of acetylene when adsorbed on the surface, and  ${}^1E_0$  is the ground state energy at the optimized free molecular geometry. In the case of acetylene, Table I, the  $E^{\text{int}}$  energy ranges from 101 kcal/mol to 107 kcal/mol for the different surfaces studied. Averaging the corresponding values we obtain 103 kcal/mol, which is twice the carbon–copper single bond energy for these systems.

## B. Ethylene

We find the same trends for ethylene, as for acetylene, but the variations in the C–C distance and in the bending angle upon adsorption are more disperse (see Table II and Fig. 2). For the (111) cross-bridge adsorption site the increase of the C–C bond length is 0.18  $\text{\AA}$  giving a distance of 1.51  $\text{\AA}$ , which is close to the single-bond C–C distance in ethane (1.536  $\text{\AA}$ ). For the other surfaces the elongations of the C–C bond are smaller; in the (110) case the C–C distance becomes 1.39  $\text{\AA}$ , while for the (100) the value is 1.46  $\text{\AA}$ , see Figs. 3 and 4. In particular, for the (111) surface in the di- $\sigma$  absorption site the C–C distance remains almost unperturbed with respect to the gas phase; this fact is also reflected in the low value of the computed chemisorption energy, 5 kcal/mol, which, together with the unperturbed structure, is typical for a physisorbed state.

Examining the triplet state of the gas phase ethylene molecule in Table II, we find two main conformations; the staggered (twisted) and the eclipsed. The eclipsed conforma-

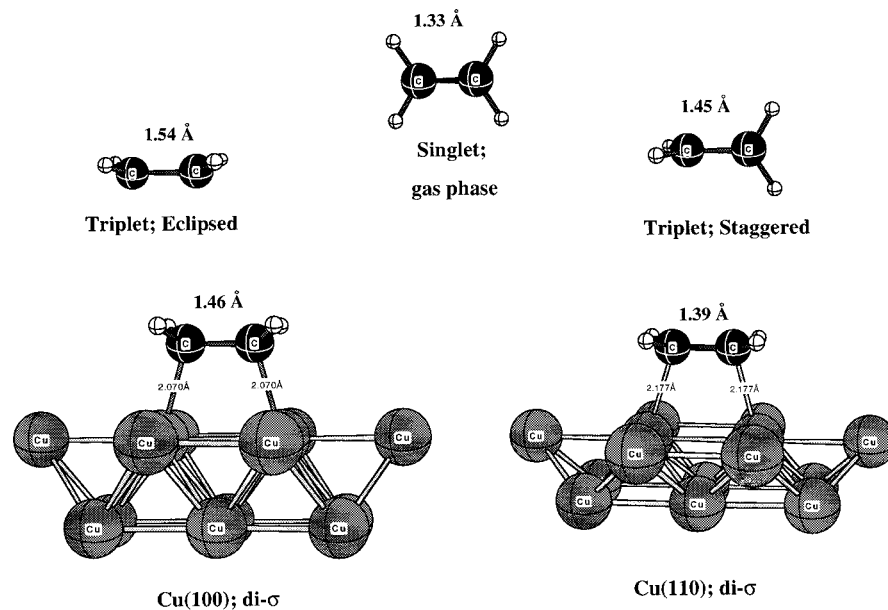


FIG. 3.  $C_2H_4$  gas phase (singlet and triplet) with  $C_2H_4/Cu(110)$  and  $C_2H_4/Cu(100)$ .

tion is actually a transition state with an imaginary frequency corresponding to the rotation into the staggered conformation. The surface-optimized structures clearly correspond to this state which will become a stable minimum on the substrate due to the rotation into the staggered conformation

being hindered on the surface. The bond-prepared, eclipsed triplet ethylene conformation is higher by approximately 19 kcal/mol than the adiabatically excited  $^3B_{1u}$  state of staggered (twisted) ethylene, but for the surface this conformation turns out to be the most appropriate.

The optimized structural parameters for the gas phase species compare very well with experimental data and with previous calculations (cf. Table II). For the excitation energy we may assess the quality of our results by comparing the computed value for the vertical excitation energy (104 kcal/mol at the B3LYP level) with the experimental 100.6 kcal/mol (Ref. 29) and a previous theoretical study at the multi-configuration SCF (MCSCF) level where a value of 98.5 kcal/mol was obtained.<sup>30</sup> The present approach is thus accurate to within a few kcal/mol which is quite sufficient for the present purposes.

Performing the division of the interaction energy into a cost for bond preparation and a gain from bond formation for the interaction of ethylene with copper surfaces, we expect a behavior similar to that of acetylene, but with the hybridization of the molecule going from  $sp^2$  (double C-C bond) to  $sp^3$  (single C-C bond). We concentrate on the (110) and the (100) surfaces [the (111) surface will be discussed separately]. Considering the computed chemisorption energies, 13 and 6 kcal/mol, together with the singlet-triplet excitation energies, 92 and 86 kcal/mol, we again find a per carbon-copper bond strength of  $\sim 53$  kcal/mol, and that the bonding is appropriately analyzed in terms of the gas phase excited triplet state. It is significant to observe that the value of 53 kcal/mol is in correspondence with the characteristic Pt-C  $\sigma$ -bond energy used by Carter and Koel<sup>7</sup> to estimate surface reaction energetics of the mechanism of ethylene decomposition on a Pt(111) surface.

In spite of the large interaction energy, manifested through the structural distortions of the adsorbate, the chemi-

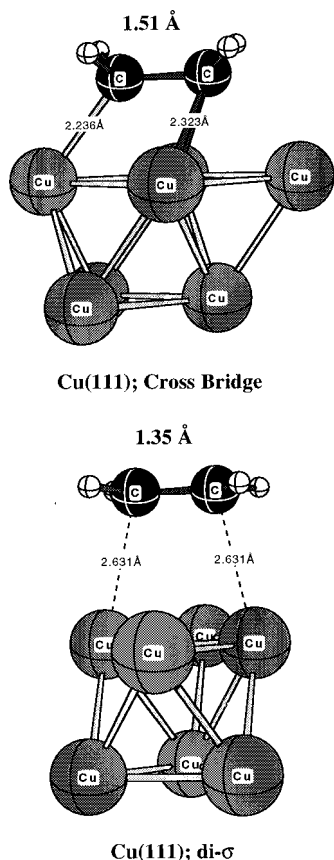


FIG. 4.  $C_2H_4$  on Cu(111); cross bridge and di- $\sigma$  adsorption sites.

TABLE III. Computed geometries (Å) and adiabatic singlet-triplet excitation energies ( $\Delta$ , kcal/mol) for benzene in optimal gas phase geometries and for the gas phase species in the surface optimized geometries. The chemisorption energies  $D_e$  (kcal/mol) are computed with respect to the bond-prepared cluster at large distance (same as the ground state). The numbering of the atoms corresponds to that in Figs. 5 and 6.

Property	Gas phase			Chemisorbed geometry	
	Singlet	Triplet		Quinoid form less distorted	
		Quinoid	Antiquinoid	(110)	(110)
C <sub>1</sub> -C <sub>6</sub>	1.40 (1.397) <sup>a</sup>	1.47 (1.47) <sup>b</sup>	1.39	1.45	1.42
C <sub>6</sub> -C <sub>4</sub>	1.40 (1.397) <sup>a</sup>	1.34 (1.37) <sup>b</sup>	1.52	1.39	1.43
C-H	1.08 (1.084) <sup>a</sup>	1.08 (1.07) <sup>b</sup>	1.09	1.09	1.09
Cu <sub>23</sub> -C <sub>4</sub>	...	...	...	2.31	2.21
Cu <sub>22</sub> -C <sub>1</sub>	...	...	...	2.34	...
Z <sup>C<sub>1</sub></sup> <sup>c</sup>	...	...	...	1.89	2.05
Z <sup>C<sub>6</sub></sup> <sup>d</sup>	...	...	...	2.05	2.05
C <sub>1</sub> C <sub>6</sub> C <sub>4</sub>	120.0	120.4	119.4	120.7	120.2
C <sub>3</sub> C <sub>1</sub> C <sub>6</sub>	120.0	118.9	121.2	117.0	119.5
C <sub>4</sub> C <sub>6</sub> C <sub>1</sub> C <sub>3</sub>	0.0	5.0	0.0	7.4	0.4
H <sub>7</sub> C <sub>1</sub> C <sub>6</sub> C <sub>4</sub>	0.0	5.3	0.0	17.5	5.3
H above ring	0.0	2.3	0.0	17.5	17.6
$\Delta$	0	90	89	98	102
$D_e$	...	...	...	18	14

<sup>a</sup>Experimental data from Ref. 48.

<sup>b</sup>Multiconfiguration SCF results from Ref. 49.

<sup>c</sup>Z<sup>C<sub>1</sub></sup>=C<sub>1</sub> height above the surface.

<sup>d</sup>Z<sup>C<sub>6</sub></sup>=C<sub>6</sub> height above the surface.

sorption energies are small due to the large excitation energy required to rehybridize the adsorbate.<sup>9</sup> The chemisorption energy of ethylene on Cu(100) has been determined experimentally from temperature programmed desorption (TPD) studies by Jenks *et al.*<sup>31</sup> giving a value of  $8 \pm 2$  kcal/mol. Our computed value, 6 kcal/mol, for this surface thus agrees quite well, but it should be noted that a larger error bar must be assigned to this value in the absence of results for a larger sequence of cluster models.

For the Cu(111) surface model we must again consider the preparation of the cluster for bonding. Both the acetylene and ethylene molecules require two open shells on the cluster to form local covalent bonds to the adsorbate. For the cross-bridge site on the Cu(4,3) cluster we find a negative chemisorption energy (unbound by 11 kcal/mol) when computed with the cluster doublet ground state as reference. The 30 kcal/mol bond-preparation cost for the cluster would lead to a chemisorption energy of 19 kcal/mol, but again this large correction cannot be regarded as improving the model. In fact, using instead the larger Cu<sub>19</sub> cluster with its 9 kcal/mol correction gives a directly computed chemisorption energy of -25 kcal/mol, which after correction results in a computed chemisorption energy of -16 kcal/mol. It should be noted that ethylene experimentally does not bind to the Cu(111) surface and even though the computed chemisorption energy corresponds to an unbound state the distortion of the molecule is the largest at this chemisorption site.

### C. Benzene

The chemisorption of benzene has been studied experimentally for several transition metal substrates including

Pd(111),<sup>32,33</sup> Rh(111), Pt(111),<sup>34</sup> Ni(111),<sup>35</sup> Ni(100),<sup>36</sup> Cu(111),<sup>37</sup> and Cu(110).<sup>36,38,39</sup> Determinations of the chemisorbed geometry on Pd(111), Rh(111), and Pt(111) (Ref. 34) indicate an increase of the ring radius upon adsorption accompanied by a distortion leading to unequal bond lengths in the ring. There are even indications of a distortion of the carbon backbone into a boatlike structure on Pt(111) (Ref. 34) as well as on Ni(110),<sup>40</sup> but the obtained distortions are small and well within the experimental errors.<sup>40</sup> On Ni(111) it seems clear that, rather than distorting the benzene molecular backbone, the system prefers to rearrange the substrate atoms.<sup>35</sup> Lomas and Pacchioni<sup>41</sup> performed a theoretical study of the interaction of benzene with the Cu(110), Cu(111), and Pd(111) surfaces, and in particular the effects of coadsorbing chlorine. The calculations were performed at the Hartree-Fock level and only weak physisorption was found, and thus no distortions of the geometry were reported. In our present work we have optimized the structure of benzene on rather large (Cu<sub>13</sub>) all-electron cluster models of the Cu(110) and Cu(100) surfaces. The level of calculation, DFT with gradient-corrected exchange-correlation functionals, is higher and, of the two structures obtained, one (the lowest energy conformation) shows significant distortions of the carbon backbone for chemisorption on the Cu(110) surface. For the (100) surface we have only found physisorbed structures with no significant distortions.

Table III displays results for geometries, triplet excitation energies, and binding energies for benzene, which we use to conduct a similar type of conformational analysis as for acetylene and ethylene (see Figs. 5 and 6). In the gas phase there are two known low-lying excited triplet states of

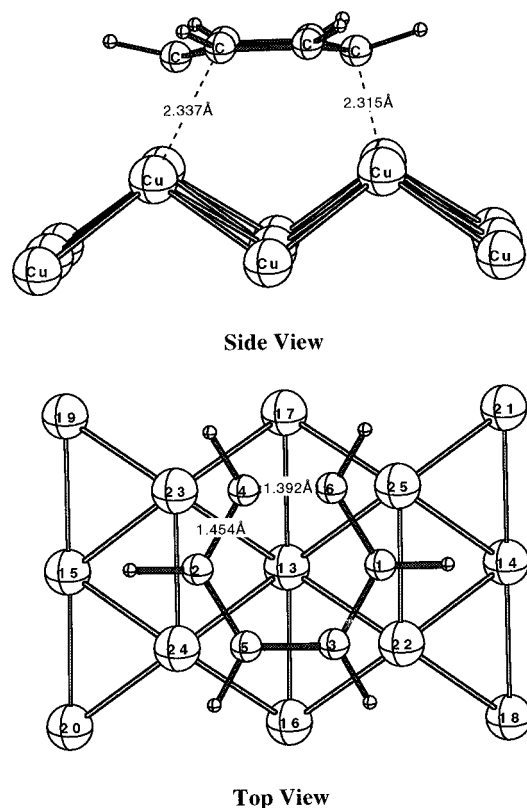


FIG. 5. Optimal geometry for adsorption of  $C_6H_6$  on Cu(110). Quinoid form.

benzene with computed excitation energies of about 90 kcal/mol. These triplet states correspond to excitations from the highest,  $1e_{1g}$ , orbital into each of the two components of the unoccupied  $e_{2u}$  LUMO orbital. This results in two different  $C_{2v}$  distortions of the molecule leading to the quinoid (four long and two short bonds) or the antiquinoid structure (four short and two long bonds), both with nearly the same excitation energy. The quinoid structure is bond-prepared in the para-position, while the antiquinoid form has its radical character concentrated on the two longer bonds at the "waist of the molecule." Since each C–Cu bond to the surface has a bond strength of about 50 kcal/mol (see the results on acetylene and ethylene, above) the required excitation energy of 90 kcal/mol can be compensated by the formation of two covalent bonds to the surface for each of these systems. We have attempted to find a bond-prepared quintet state as well, but the lowest quintet state has an excitation energy above 200 kcal/mol and has a chair structure which does not permit the formation of the four C–Cu bonds that would be required to counteract the high excitation energy.

The lowest energy optimized structure found on the Cu(110) surface shows the distortions characteristic of the quinoid excited triplet state; the molecule tends toward a boat conformation with a slight bending up of the hydrogens, both in the gas phase and on the surface. In spite of the large stability of the ground state benzene molecule we find a surprisingly low (8 kcal/mol) sensitivity to the additional distortions required to move the molecule from the gas phase op-

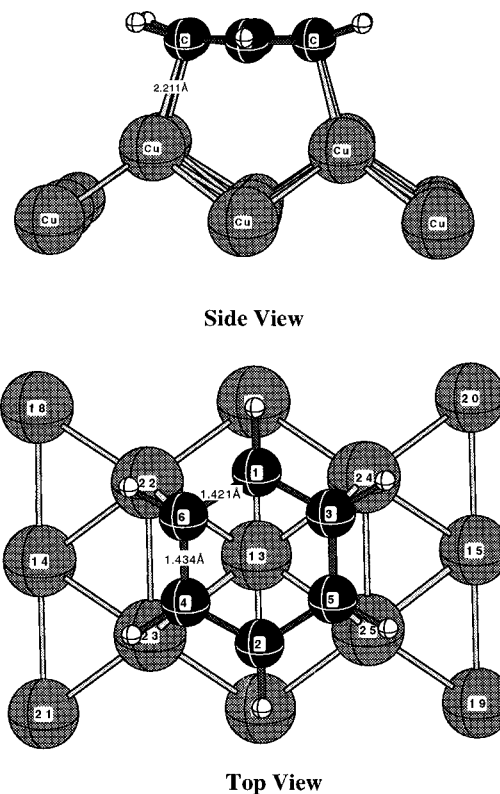


FIG. 6. Optimal geometry for adsorption of  $C_6H_6$  on Cu(110). Less distorted.

timal quinoid structure to that actually optimized on the cluster. The computed chemisorption energy is 18 kcal/mol which, if compared to the 98 kcal/mol excitation energy to the triplet quinoid structure, gives a total interaction energy of 116 kcal/mol or a C–Cu per bond energy (assuming two covalent bonds formed) of 58 kcal/mol. For the planar, only slightly distorted, structure the results are similar, with a somewhat smaller resulting chemisorption energy (Table III). Accepting the uncertainties in evaluating chemisorption energies from a single cluster, we find a per bond strength very similar to what was found for acetylene and ethylene. Finally, we note that for the (100) surface we have only found physisorbed benzene, with no significant distortions from the gas phase ground state structure.

#### IV. DISCUSSION

Experimental data, e.g., NEXAFS, LEED, and photoelectron diffraction data, indicate a significant elongation of C–C distances and a reduced bond order upon adsorption of unsaturated hydrocarbons on copper surfaces, for instance ethylene and acetylene enlarge their C–C bonds by 0.10 and 0.26 Å, respectively, when adsorbed on a Cu(111) surface.<sup>40</sup> There are indications that the same happens with benzene; both the resonance structure and the planarity might be broken upon adsorption, results which according to Ref. 40, however, remain statistically insignificant. It is therefore interesting to note that the present DFT calculations for chemisorbed benzene indeed indicate that large changes can occur

in the adsorbate structure and that the  $\sigma$ - $\pi$  separability is corrupted by breaking the planar symmetry. This is furthermore in agreement with recent XES and NEXAFS data,<sup>42</sup> which for the Ni(100) surface show a large mixing of  $\sigma$  and  $\pi$  states that could indicate a breaking of the planar symmetry of the molecule. For Cu(110) much less such mixing is observed, in contradiction to our optimized structure; this point will be returned to below.

The presently investigated molecules thus exemplify that large changes can occur in the structure of adsorbate molecules, yet the binding energy with the surface is comparatively weak. We find by comparing reactant geometries, bonding energies and triplet excitation energies, that this fact implies an adsorption process that includes a simultaneous spin-uncoupling in the adsorbate and the substrate, which, for each of the subsystems, corresponds to an excitation to the triplet state. Thus, a large part of the available energy is spent for an intrasystem (singlet to triplet) excitation which leads to a rehybridization of the organic adsorbate molecule so preparing for the bonding. The molecule "realizes" its possibility to organize chemical bonds with the metal atoms which carry a high spin density. For the extended surface the required excitation of the metal to the bond-prepared (local) triplet state is expected to occur with a low energy cost, while for particular clusters modeling the substrate a high excitation energy may be required both for the adsorbate and for the cluster to make both components bond-prepared.

The picture of an involvement of an excited state has been partly investigated earlier by both Hermann and co-workers<sup>9,10</sup> and by Clotet and Pacchioni,<sup>11</sup> but without explicitly indicating the state involved. In fact, both groups have for certain cases investigated the path from gas phase to chemisorbed molecule and have obtained barriers to form the chemisorbed state in the case of ethylene on Cu(111) (Ref. 10) and acetylene on the same surface,<sup>11</sup> in the latter study the interaction with the Pd(111) surface was also investigated and the absence of a barrier explained as due to the much smaller repulsion against the Pd  $sp$ -band than against the more strongly occupied valence band in Cu. We will discuss these previous results in the light of the present findings and proposed interaction mechanism.

Both groups of Refs. 10 and 11 use the Cu<sub>7</sub>(4,3) cluster to model the Cu(111) surface; this particular cluster has an unusually large excitation energy, 30 kcal/mol, to reach the bond-prepared state, i.e., the quartet state. This means that, in moving the molecule towards the surface in a simulation of the chemisorption process, the final end point, the chemisorbed state, will be artificially higher in energy by this amount. This should be corrected for in a comparison between the free and the chemisorbed system. In Ref. 10 two, essentially physisorbed, minima are found separated by a barrier of about 8 kcal/mol. The calculations were performed at the local density (LDA) level, which is known to give systematically excess binding energies, but it was assumed that different points on the surface would show similar errors. In our work we have used gradient-corrected functionals, both for the geometry optimizations and for the energy evaluations. Recomputing the energies at the LDA level we

find a differential overbinding of the inner minimum (cross-bridge; Table II) by 8 kcal/mol over the di- $\sigma$  physisorbed state. Correcting for this overbinding we find the cross-bridge structure unbound by 11 kcal/mol as reported in Sec. III B, which, with the cluster correction, would become bound by some 19 kcal/mol. As discussed previously, such a large correction is unreliable and going to a substantially larger cluster (Cu<sub>19</sub>) with a lower excitation energy actually also leads to the inner state being strongly unbound; i.e., a very different picture from that in Ref. 10. We would also expect the barrier height for this path to be somewhat underestimated through the use of the LDA, but the main point for the present discussion is the existence and origin of the barrier.

Clotet and Pacchioni<sup>11</sup> performed a similar study on the adsorption of acetylene on the (111) surface of both Cu and Pd. At the Hartree-Fock level they report consistently very large cluster size corrections; even for the largest Cu<sub>22</sub> cluster the correction amounts to some 88 kcal/mol which is much larger than expected for a cluster of this size. Without using bond-prepared cluster states in the evaluation of the chemisorption energies the acetylene molecule remains strongly unbound, by 38–42 kcal/mol, even for the largest cluster. Chemisorption on the Pd<sub>7</sub> cluster, on the other hand, results in consistently too large binding energies. Correlation was introduced through MP2 for the smallest Cu<sub>4</sub> and Pd<sub>4</sub> clusters which lead to a directly computed chemisorption energy for copper in good agreement with experiment while the binding energy to the Pd cluster was grossly overestimated at 124–148 kcal/mol. This poor result was interpreted as due to that the interaction with Pd<sub>4</sub> may not be representative for the interaction with a Pd(111) surface. Besides, it is well known that at the Hartree-Fock level the electronic structure of small Pd clusters exaggerates the contribution of the  $4d^{10}$  configuration compared to  $4d^9 5s^1$ . This probably gives a Pauli repulsion that is too small and a binding that is too large.<sup>43</sup> It should be noted that the structures obtained in our present work and those of Clotet and Pacchioni for the Cu clusters are still in good agreement.

Clotet and Pacchioni furthermore computed the interaction curves for the adsorbate optimized at different heights above the surface and obtained a barrier in the case of Cu(111), but found no barrier for chemisorption on the Pd(111) surface. In their analysis of the contributions to the interaction energies they found a substantially larger repulsion against the  $4sp$  valence band in the case of copper than for the Pd surface. This was indicated as the origin of the barrier to chemisorption on Cu(111). Building on their findings and those of Hermann and co-workers<sup>10</sup> we propose an explicit assignment of the states involved in the creation of the barrier. The picture, illustrated in Fig. 7, is one of molecular spectroscopy, where the state which forms the excited state at long distance, of the same symmetry as the ground state, interacts at shorter distance with the lower state to form an avoided crossing and thereby becomes the ground state.

The electronic states involved to form the upper state at long distance are the triplet state of the adsorbate molecule and an electronic state of the substrate with at least two open

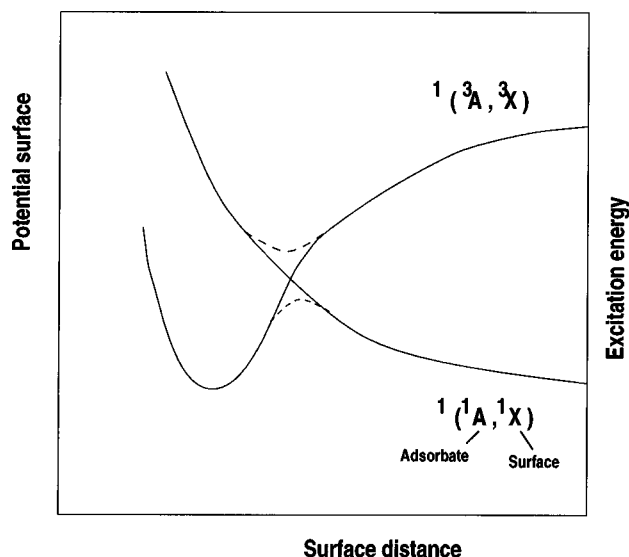


FIG. 7. Butadiene eclipsed geometry.

shells of the appropriate symmetry and localized on the appropriate atoms. These states will be spin-coupled to give the same overall spin and state symmetry as the lower state (ground state) at long distance. There is thus no spin-orbit coupling involved, simply the recoupling of the spins in each reactant prior to forming new, spin-coupled orbitals, but now with the spin-coupling appropriate to two covalent bonds between adsorbate and substrate. It should be noted that singlet-triplet transitions in organic molecules are strongly forbidden, since spin-orbit coupling in such species is almost negligible.<sup>30,44,45</sup> The proposed mechanism has thus nothing to do with the magnetic, i.e., spin-orbit coupling, interactions since there is no total spin change in the system. The spin uncoupling is rather due to the exchange interaction.

It is assumed that, in the chemisorption process, the required localized surface states are induced during the adsorption reaction at a low energy cost and that the "choice" of active atoms (i.e., where the spins localize) is determined by geometry constraints in the adsorbate organic molecule and by the surface arrangement in the direction of approach. In terms of theoretical studies the important point is that when the energy gain from bond formation is higher than the cost of the bond preparation in terms of a singlet-triplet excitation, then indeed the bond prepared triplet state species should be assumed.

The crossing of the two states involved may or may not lead to a barrier to reach the more strongly bound state. Barriers have been found theoretically for e.g., ethylene on Cu(111) in going from the physisorbed di- $\sigma$  state to the cross-bridge structure<sup>10</sup> (unbound in the present work but weakly chemisorbed in Ref. 10) and similarly for acetylene chemisorption, also on Cu(111).<sup>11</sup> Interestingly, in the latter study no barrier was found for chemisorption onto the Pd(111) substrate, which indicates a late curve-crossing, i.e., after the new bonds have begun to form. The existence of curve-crossings and resulting barriers also for chemisorption

systems opens interesting possibilities to find different chemisorption states; one such case may be exemplified by the present optimized structure for benzene.

In a recent XES and NEXAFS study of benzene on Cu(110),<sup>42</sup> the benzene molecule was found to give rise to spectra very similar to the gas phase structure, indicating that neither geometric nor electronic structure was perturbed to any greater extent. We have computed XES, NEXAFS and shake-up spectra for the two structures that we found for the Cu(110) surface<sup>46</sup> and for different gas phase distortions leading to the distorted structure; these include planar undistorted benzene, benzene with hydrogens bent up and finally both the gas phase and chemisorbed quinoid structure. It is clear that the computed and measured spectra refer to two different species. The experiment was performed at 80 K, which would probably be too low to allow a barrier to be overcome and a trapping of the molecules in a precursor state cannot be excluded. Lambert and co-workers have investigated the kinetics of benzene formation from acetylene on Cu(110) (Ref. 38) and have, through temperature programmed reaction (TPR) experiments, deduced a reaction-controlled desorption of benzene from the substrate; benzene chemisorbed at 120 K was found to desorb at temperatures ( $\leq 280$  K) well below the 325 K required to observe desorption of benzene from the acetylene-covered surface. However, in an early paper Avery<sup>47</sup> reports observing the  $\gamma(\text{CH})$  mode of benzene as a shoulder on the corresponding signal from the adsorbed acetylene after annealing to 280 K. Thus, one possible interpretation of the TPR experiments is that reactively formed benzene is produced in the more strongly bound state at a lower temperature than deduced in the experiment. This state could thus be reachable through the reaction, but could be hindered to form from chemisorbed benzene through the existence of a barrier.

An uncertainty in the present study is the possible involvement of surface relaxation in stabilizing the adsorbate system; this has been observed experimentally in the case of benzene on Ni(111), where the adsorption induces a significant distortion of the substrate.<sup>35</sup> In the present study the distorted quinoid structure was found with a higher chemisorption energy than the less distorted planar structure, however, and inclusion of substrate relaxation should have a similar stabilizing effect on both structures. It should be noted that the reported distortions of the carbon backbone are not mainly a consequence of the interaction with the surface, but is rather the effect of the electronic excitation; very similar distortions are found for the gas phase quinoid triplet (Table III). The energy difference between the gas phase and surface optimized quinoid structures is 8 kcal/mol (Table III) such that there is no significant additional strain on the carbon backbone introduced through the buckling of the ring. Based on the gas phase quinoid structure one could thus expect some reduction of the backbone distortion through substrate relaxation, but since the optimum backbone bending angle in the gas phase triplet is around  $5^\circ$  we still expect the resulting structure to be distorted. It must again be pointed out that the large excitation energy to reach the triplet state is more than offset by the energy gain from the

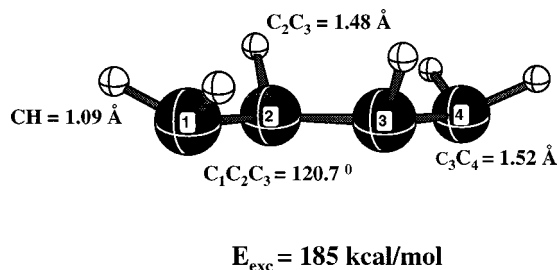


FIG. 8. Crossing potential surfaces.

covalent bonds formed. Two additional uncertainties exist in connection with the determination of what should be the most favorable structure; first, additional adsorption sites should be considered to ensure that the global minimum has been found and, second, the character of each of the stationary points should be established through frequency analysis. However, since the quinoid triplet state is a molecular state and since the excitation energy can definitely be balanced by the bondformation, we feel quite certain that this state should be formed on the substrate.

The present proposal of the explicit involvement of the excited triplet state has many implications. As mentioned in the Introduction, the  $\text{N}_2 \text{ } ^3\Sigma_u^+$  state has been identified by Freund *et al.*<sup>5</sup> as the bonding state in  $\alpha\text{-N}_2$  on Fe(111) and the idea of the involvement of the triplet excited state has already been applied in a predictive sense by Rochefort *et al.*<sup>8</sup> in their study of reaction pathways on Pd(110) and Cu(110). It has also been applied by Carter and Koel to the study of the ethylene decomposition on Pt(111).<sup>7</sup> We have used it in the present investigation to identify possible adsorption states of benzene by investigating the gas phase structures of the possible triplet states. We have furthermore investigated bond preparation of butadiene, where, through the involvement of a quintet spin state, four bonds could be prepared. One such candidate has been found (Fig. 8), with an appropriate structure and an excitation energy of 185 kcal/mol, which could still correspond to a weakly bound chemisorbed state considering the deduced carbon–copper bond strength of about 50 kcal/mol. Thus, it would seem that the search for appropriate surface structures and the analysis of strong interactions at surfaces where covalent bonds are formed or broken, can be shifted to a study of the properties of the gas phase excited states of the adsorbates, in a search for appropriately bond-prepared species.

## V. SUMMARY

In the present work we have analyzed the interaction of small unsaturated hydrocarbons (acetylene, ethylene, and benzene) with the low-index copper surfaces (111), (110), and (100). Analysis of the structures obtained for the chemisorbed systems shows strong similarities with the gas phase excited triplet states of these species. For acetylene the cis-form of the triplet state corresponds to the bond prepared state, i.e., the one which can form two covalent bonds to the substrate. For ethylene it is the eclipsed form, which in the gas phase corresponds to a transition state, which is appro-

priately bond prepared. The bond-preparation corresponds to a simultaneous spin-uncoupling in the two reactants, adsorbate and substrate, without change of the overall spin state. Thus, chemisorption, when accompanied by formation of covalent bonds, may be seen as a crossing between two electronic states which may or may not be associated with a barrier. On copper surfaces barriers have been found in earlier theoretical studies, and the existence of a barrier may have prevented the observation of the predicted quinoid type structure deriving from benzene in the triplet state.

The chemical activation in the adsorption on, e.g., metal surfaces can thus be seen as inducing spin-uncoupling in the adsorbate which corresponds to an excitation to the appropriate electronic state which prepares the adsorbate for bonding, i.e., in the present cases the triplet state. This finding opens the possibility to analyze complicated reactions from the gas phase properties of the excited states of the reactants. One interesting such example has already been given by Carter and Koel in Ref. 7.

## ACKNOWLEDGMENT

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