



ELSEVIER

Surface Science 337 (1995) 205–214

surface science

Geometry and binding of acetylene on Cu(111): ab initio cluster studies

K. Hermann ^{a,*}, M. Witko ^b^a Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, D-14195 Berlin, Germany^b Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek, 30239 Cracow, Poland

Received 22 July 1994; accepted for publication 5 January 1995

Abstract

Recent photoelectron diffraction (PED) data show that the adsorption of C_2H_2 on Cu(111) is combined with major structural changes in the adsorbate while the overall adsorbate–substrate binding is weak. These experimental findings can be explained by details of the C_2H_2 /Cu(111) chemisorption interaction as shown in the present cluster model calculations based on ab initio Hartree–Fock and correlated wave functions. Extended studies on a small $Cu_7C_2H_2$ cluster confirm that C_2H_2 stabilizes with its C–C axis parallel to the Cu(111) surface over a bridge site where the two C centers point towards adjacent 3-fold hollow sites as suggested by the PED data. In the calculations the optimized C–C distance of adsorbed C_2H_2 is increased by 0.16 Å with respect to that of the free molecule which is close to the experimental increase (0.28 ± 0.10 Å). Further, in the cluster model the C–H axes are found to tilt by 60° with respect to the C–C axis pointing away from the surface (hydrogen positions could not be obtained from PED). As a result, the overall weak C_2H_2 –Cu(111) interaction is determined by a competition between energy required to change the geometry in the adsorbate molecule and energy gained due to local bond formation of the distorted molecule. The latter contribution can be connected with binding mechanisms which are well known from organometallic chemistry. Finally, the present model results suggest strongly that correlation contributions to binding are necessary for a correct evaluation of the energetics of the C_2H_2 /Cu(111) system.

Keywords: Ab initio quantum chemical methods and calculations; Chemisorption; Clusters; Copper; Hydrocarbons; Low index single crystal surfaces; Models of surface chemical reactions; Surface chemical reaction

1. Introduction

The adsorption of small molecules at substrate surfaces is of considerable interest from both experimental and theoretical points of view. It forms elementary steps in many important surface processes

such as corrosion and coating as well as in heterogeneous catalytic reactions [1–3]. A microscopic description of the adsorption process must be based on realistic surface interaction mechanisms which derive conceptually from two contributions, (a) those of local adsorbate–substrate binding and (b) those of changes in the intra-molecular binding of the adsorbate. Amongst the variety of local adsorbate–substrate binding schemes discussed at present [4] there are mainly three different types, (a) ionic surface

* Corresponding author.

binding as found for oxygen adsorption at alkali metal surfaces [5–8] where electrostatic contributions dominate the interaction, (b) covalent or dative binding as found for hydrogen adsorption at semiconductor surfaces [9] or for CO adsorption at transition metal surfaces [10,11] where orbital hybridization becomes important, and (c) van der Waals binding as found for xenon physisorption at metal surfaces [12] where polarization determines the overall weak bond. Binding energies connected with these binding schemes have to be combined with those from changes in the intra-molecular adsorbate binding to yield energies characterizing the global surface interaction of the molecular adsorbate.

In many cases, molecular adsorption is accompanied by only minor effects on the intra-molecular electronic structure. As a consequence, the adsorbing molecule remains mostly unchanged in its geometry and an overall weak surface interaction reflects weak local adsorbate–substrate binding. This contrasts to systems where the adsorption process leads to a major geometric rearrangement in the adsorbing molecule and changes its intra-molecular binding. Here intra-molecular energy contributions cannot be neglected and the global surface interaction of the molecular adsorbate may not characterize the local adsorbate–substrate bond formation. Extreme cases of this type are dissociative adsorption systems where the adsorbate loses its identity near the surface [5,7]. Other examples include systems where the geometric rearrangement in the adsorbing molecule requires energy which partially compensates the energy gain due to local bond formation between the distorted adsorbate molecule and the substrate surface (competitive binding). As a result, the global surface interaction of the molecular adsorbate may be weak while it cannot be described by van der Waals type physisorption.

Experimental results for acetylene, C_2H_2 , adsorption at 3d metal surfaces [13,14] identify a rather weak adsorbate–substrate interaction. In fact, the $C_2H_2/Cu(111)$ adsorption system has to be cooled to rather low temperatures to stabilize acetylene near the substrate [13,14]. However, recent photoelectron diffraction (PED) experiments show a major structural rearrangement in C_2H_2 upon adsorption at the Cu(111) surface [13]. The molecule which is linear in gas phase is observed to stabilize over an fcc

(111) bridge site where the C–C axis points almost parallel to the surface and the two C centers are located near two adjacent 3-fold hollow (fcc and hcp) sites. This results in a C–C distance, $d_{C-C} = 1.48 \pm 0.10$ Å, of the adsorbate which is greatly increased with respect to that of the free molecule, $d_{C-C} = 1.20$ Å. The hydrogen positions of adsorbed C_2H_2 cannot be observed in the experiment due to their small scattering cross section [13]. Overall, the $C_2H_2/Cu(111)$ adsorbate system seems a possible candidate for a surface interaction which is determined by competitive contributions as discussed above.

Theoretical cluster studies on the C_2H_2 /metal adsorption system have been published in the literature using both semiempirical [15,16] and ab initio [17,18] techniques. In these studies based on very small $C_2H_2Me_n$, $Me = Fe, Ni, Cu$, $n = 1-3$, model clusters different adsorbate sites have been considered and the adsorbate geometry was varied within a limited range. The authors conclude [18] for distorted C_2H_2 (enlarged C–C distance, CH ends bent by 30°) adsorbing at Cu_2 and Cu_3 clusters respectively that the local adsorbate–substrate bond can be described by a Dewar–Chatt–Duncanson-type donation mechanism [19,20]. This mechanism is well known from organometallic chemistry [21] and weakens the C–C bond of the adsorbate. Further, occupied Cu d orbitals are found to interact strongly with C_2H_2 valence orbitals resulting in an additional repulsion which weakens the adsorbate–substrate bond. Unfortunately, neither absolute binding energies nor C_2H_2 distortion energies could be given in the ab initio studies [18] and the most stable adsorbate site and geometry for $C_2H_2/Cu(111)$ was not identified from total energy optimizations.

In the present work we have examined the detailed binding energetics of C_2H_2 adsorbing at the Cu(111) surface based on cluster models. Calculations using ab initio Hartree–Fock as well as correlated (CI) wave functions are carried out for a $Cu_7C_2H_2$ cluster where the Cu_7 substrate geometry was taken from the ideal Cu(111) surface while the C_2H_2 adsorbate species was geometry optimized using the experimentally [13] identified C_s symmetry as a constraint. The calculations yield C_2H_2 to stabilize at the Cu_7 substrate cluster with its C–C axis almost parallel to the surface and a C–C dis-

tance increased by 0.16 Å close to the experimental findings [13]. In addition, the CH ends of the adsorbate are found to be bent by about 60° with respect to the C–C axis and pointing away from the surface. This adsorbate geometry reflects local equilibrium at both Hartree–Fock and CI levels and the respective $\text{Cu}_7\text{C}_2\text{H}_2$ CI total energy lies 0.15 eV below that of the separated Cu_7 and C_2H_2 subunits (with C_2H_2 at its linear free molecule geometry). This suggests that stabilizing C_2H_2 at the $\text{Cu}(111)$ surface gains only small amounts of energy indicative of a weak adsorbate–surface interaction which is consistent with experiment. A detailed energy analysis reveals the origin of the overall weak interaction as a partial compensation of two competing contributions. First, the adsorbing C_2H_2 molecule has to be restructured by increasing its C–C distance and bending its CH ends. The energy required for these structural changes is estimated to be 1.0–1.5 eV based on calculations on the free molecule. Second, in the distorted

molecule the C 2sp-type orbitals can undergo a rehybridization such that Cu–C bonds can be formed. This local bond formation must gain 1.0–1.5 eV to overcompensate the distortion energy of the C_2H_2 adsorbate. Its origin is described by a rehybridization leading to a weakening of the C–C triple bond in C_2H_2 and offering modified adsorbate orbitals which can couple with the substrate via a Dewar–Chatt–Duncanson-type donation/backdonation mechanism [19,20]. While the binding of the distorted molecule with the surface has been discussed previously [15–18] for small clusters the present work shows that the distortion energy of the adsorbate has to be included to obtain a reliable description of the binding energetics in the $\text{C}_2\text{H}_2/\text{Cu}(111)$ adsorbate system. Further, the present model results suggest strongly that correlation contributions to binding are necessary for a correct evaluation of the energetics of the present system.

In Section 2 we describe briefly computational

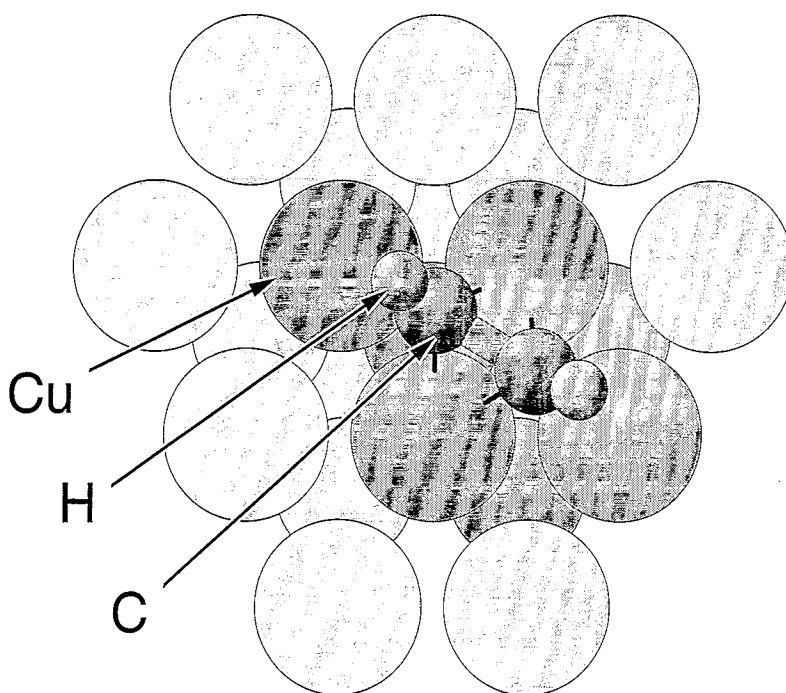


Fig. 1. Geometric structure of the $\text{Cu}_7(4, 3)\text{C}_2\text{H}_2$ cluster used in the present study. The C_2H_2 adsorbate is assumed to bend over a $\text{Cu}(111)$ bridge site with the two C centers pointing towards adjacent fcc and hcp hollow sites. The very light balls represent peripheral Cu substrate atoms which together with $\text{Cu}_7(4, 3)\text{C}_2\text{H}_2$ form $\text{Cu}_{22}(12, 7, 3)\text{C}_2\text{H}_2$ used in preliminary test calculations.

methods and details of our models while Section 3 presents the numerical results and discussion. Finally, section 4 summarizes conclusions from the present study.

2. Theoretical details

The present study uses a $\text{Cu}_7(4, 3)\text{C}_2\text{H}_2$ cluster of C_s symmetry, see Fig. 1, to model the $\text{C}_2\text{H}_2/\text{Cu}(111)$ adsorbate interaction where the Cu_7 substrate part forms a section of the ideal $\text{Cu}(111)$ surface with four atoms of the first and three atoms of the second layer and the Cu–Cu nearest neighbor distance is taken from the bulk, $d_{\text{Cu–Cu}} = 4.80$ bohr. The adsorbate geometry of the $\text{Cu}_7\text{C}_2\text{H}_2$ cluster is optimized in the calculations by varying all atom center positions of C_2H_2 along the C_s symmetry plane of the cluster (containing adjacent fcc and hcp hollow surface sites) such that the adsorbate bends symmetrically over the $\text{Cu}(111)$ bridge site in accordance with experimental results [13]. For this geometry the Cu_7 substrate part represents a compact environment about the adsorption site which has been found necessary to give a reliable description of electronic properties of different adsorbate systems [22–24]. The optimization constraints allow for variations of four geometry parameters in the $\text{Cu}_7\text{C}_2\text{H}_2$ cluster, the C–C distance, $d_{\text{C–C}}$, the C–H distances, $d_{\text{C–H}}$, the C–C–H bending angle θ of the adsorbate ($\theta = 0$ refers to linear C_2H_2), and the adsorbate–substrate distance quantified by the normal coordinate, z , between the C–C axis of C_2H_2 and the first Cu surface layer. Test calculations showed a rather weak dependence of the adsorbate–substrate interaction on $d_{\text{C–H}}$. Therefore, this parameter was not included in the cluster optimization and fixed at $d_{\text{C–H}} = 1.999$ bohr as obtained from Hartree–Fock optimizations on the free C_2H_2 molecule. Further, cluster geometry optimizations where the assumption of the C_2H_2 C–C axis pointing parallel to the surface was relaxed yielded bending angles of less than 2° with respect to the parallel geometry. Thus, only the parallel geometry will be considered in the following. The detailed structure of the $\text{Cu}_7(4, 3)\text{C}_2\text{H}_2$ cluster as shown in Fig. 1 includes also peripheral Cu substrate atoms (very light balls) which together with $\text{Cu}_7(4, 3)\text{C}_2\text{H}_2$ form

$\text{Cu}_{22}(12, 7, 3)\text{C}_2\text{H}_2$. This cluster is used in preliminary calculations to test the cluster size dependence of the present results.

Electronic wave functions of the clusters are calculated with the ab initio Hartree–Fock (HF) LCAO method and using valence configuration interaction (CI) [25] based on the modified coupled pair functional (MCPF) approach [26] to account for correlation. Correlation contributions to cluster binding turn out to be essential for the present system as the overall interaction energy is rather small and corresponds to global stabilization only at the CI level. Further, the importance of basis set superposition errors (BSSE) is estimated using the full counterpoise method [27] and is found to yield sizable energy contributions which do, however, not affect the qualitative conclusions. The contracted Gaussian basis sets for the adsorbate atoms are all-electron type, C (9s, 5p/4s, 3p) [28] and H (4s, 1p/2s, 1p) [29], while different basis sets are used for the Cu substrate atoms. The four Cu atoms of the first surface layer surrounding the adsorption site, see Fig. 1, are described by all-electron (12s, 8p, 5d/5s, 4p, 1d) [30] basis sets while the more peripheral Cu atoms are accounted for by 4sp (6s, 1p/4s, 1p) valence bases with the $\text{Ar}/3d^{10}$ core approximated by an effective core potential (ECP) based on the frozen orbital ECP approach [31,32].

The symmetry group common to all clusters is C_s , cf. Fig. 1, and all electronic states are calculated based on C_s symmetry even if their proper symmetry was higher like for C_2H_2 which is characterized by $D_{\infty h}$ (linear geometry) or by C_{2v} (bent geometry). This results in ground state configurations $^2A'$ ($37a'^1 23a''^2$) for $\text{Cu}_7(4, 3)$ where the Ar core of the four Cu surface atoms close to the adsorbate site corresponds to $^1A'$ ($23a'^2 13a''^2$). The ground state configuration of C_2H_2 is $^1A'$ ($6a'^2 1a''^2$) {corresponding to 1A_1 ($4a_1^2 2b_1^2 1b_2^2$) in C_{2v} and $^1\Sigma_g$ ($3\sigma_g^2 2\sigma_u^2 1\pi_u^4$) in $D_{\infty h}$ symmetry} while its lowest excited triplet state is characterized as $^3A'$ ($6a'^1 7a'^1 1a''^2$). This leads to a $^2A'$ ($43a'^1 24a''^2$) ground state for $\text{Cu}_7(4, 3)\text{C}_2\text{H}_2$. In order to estimate the importance of Cu d electrons for direct binding and correlation contributions in the clusters test calculations have been performed where all Cu atoms in $\text{Cu}_7(4, 3)\text{C}_2\text{H}_2$ are described by $\text{Ar}/3d^{10}$ effective core potentials and only Cu 4sp electrons are explicitly included in the substrate wave

Table 1
Adsorbate binding parameters of the $\text{Cu}_7(4, 3)\text{C}_2\text{H}_2$ cluster

$d_{\text{C-C}}$ (bohr)	θ (Deg)	z_{min} (bohr)		D (eV)	
		HF	CI	HF	CI
(a) Full optimization					
2.58	60	3.18	3.18	0.71	−0.27
(b) Restricted optimization					
2.27	0	(3.28)	(3.28)	3.70	2.39
2.27	50	(3.28)	(3.28)	1.50	0.59
2.27	60	3.28	3.28	1.55	0.64
2.27	70	(3.18)	3.18	1.96	1.05
2.77	0	(3.28)	(3.28)	5.31	3.73
2.77	50	3.28	3.18	1.18	0.06
2.77	60	3.18	3.18	0.94	−0.12
2.77	70	3.18	3.08	0.99	−0.04

For detailed definitions of the adsorbate C–C distance, $d_{\text{C-C}}$, C–C–H angle θ , equilibrium distance z_{min} and interaction energy D see text. Part (a) shows results of the full optimization while part (b) gives the result from restricted optimizations for selected (fixed) $d_{\text{C-C}}$ and θ values. Data denoted by “HF” refer to Hartree–Fock results while those denoted by “CI” give data of the correlated calculation. Positive D values denote energies required to stabilize the adsorbate (repulsion) while negative values refer to energy gain (attraction). Further, z_{min} values enclosed in parentheses are used for the evaluation of D while the respective interaction curves do not exhibit a local minimum.

function. This corresponds to a ground state configuration $^2\text{A}'$ ($3\text{a}'^1 1\text{a}''^2$) for $\text{Cu}_7(4, 3)$ and $^2\text{A}'$ ($9\text{a}'^1 2\text{a}''^2$) for $\text{Cu}_7(4, 3)\text{C}_2\text{H}_2$.

3. Results and discussion

Table 1 lists adsorbate binding parameters for the $\text{Cu}_7(4, 3)\text{C}_2\text{H}_2$ cluster where the C_2H_2 center approaches at a $\text{Cu}(111)$ bridge site, see Fig. 1. Part (a) gives the result of the full optimization. In addition, part (b) shows results from a few restricted optimizations where the C–C distance $d_{\text{C-C}}$ and the C–C–H bending angles θ of the C_2H_2 adsorbate are kept fixed and the perpendicular adsorbate–substrate distance z is energy-optimized to yield z_{min} . The C_2H_2 – Cu_7 interaction energy D is defined by the minimum total energy difference

$$D = E_{\text{tot}}(\text{Cu}_7\text{C}_2\text{H}_2; d_{\text{C-C}}, \theta, z_{\text{min}}) - E_{\text{tot}}(\text{Cu}_7) - E_{\text{tot}}(\text{C}_2\text{H}_2), \quad (1)$$

varying $d_{\text{C-C}}$, θ , and z simultaneously (part (a)) or varying z for given $d_{\text{C-C}}$, θ (part (b)) where the

difference is taken with respect to total energies $E_{\text{tot}}(\text{Cu}_7)$, $E_{\text{tot}}(\text{C}_2\text{H}_2)$ of the separated neutral components. Values denoted by “HF” in Table 1 refer to Hartree–Fock data while those denoted by “CI” give data of the correlated calculation. Obviously, negative D values refer to adsorbate–substrate stabilization while positive values denote an overall energetically unfavorable adsorbate system where local minima z_{min} suggest only metastable equilibrium. The total energy curves are found to be rather flat about their local equilibrium geometries which makes an accurate determination of z_{min} in the constrained optimizations somewhat difficult. Therefore, the z_{min} values in Table 1 are given with a numerical error of 0.1 bohr only. For some values $d_{\text{C-C}}$, θ the total energy curves are repulsive without exhibiting a local minimum. In these cases the z_{min} entries of Table 1 are enclosed in parentheses and refer to typical distances z found as (metastable) equilibrium distances for other angles θ .

The results of the full adsorbate geometry optimization on $\text{Cu}_7\text{C}_2\text{H}_2$, Table 1a, reveal two important geometric effects. First, the adsorbed molecule has its C–C distance increased with respect to the free C_2H_2 distance ($d_{\text{C-C}} = 2.27$ bohr) which is consistent with experiment. Second, the CH ends of the adsorbate are bent by $\theta = 60^\circ$ compared to $\theta = 0^\circ$ for the (linear) free molecule. While this adsorbate geometry reflects local energy minima at both Hartree–Fock and CI levels the Hartree–Fock interaction energy D is always positive indicating only metastable equilibrium. In contrast, the optimized adsorbate geometry yields in the correlated calculations a negative D value of -0.27 eV which suggests overall weak attractive adsorbate–substrate interaction in consistence with experiment and which emphasizes the importance of correlation contributions for the evaluation of correct interaction energies in the present system. The structural changes in the adsorbing C_2H_2 molecule and their energetic consequences become already obvious in an examination of the results from restricted optimizations listed in Table 1b. If the C–C distance is fixed at its free molecule value $d_{\text{C-C}} = 2.27$ bohr the interaction energy D is always positive at both Hartree–Fock and CI levels. However, it can be lowered by bending the CH ends of the C_2H_2 adsorbate away from the surface where bending angles $\theta \approx 60^\circ$ lead to a

minimum of D . An increase of the adsorbate C–C distance to $d_{\text{C–C}} = 2.77$ bohr, equal to the lateral distance between the fcc and hcp hollow sites at the Cu(111) surface, results in a further lowering of D at bending angles $\theta \approx 60^\circ$ but still positive D values at the Hartree–Fock level. If valence correlation is included in the calculations the increased C–C distance and CH bending in the adsorbate can lead to small negative interaction energies D as shown in the CI results of Table 1b which reflects also the result of the full adsorbate geometry optimization.

In order to study the importance of Cu substrate d electrons and their correlation for the adsorbate–substrate binding additional test calculations are carried out on $\text{Cu}_7(4, 3)\text{C}_2\text{H}_2$. Here all Cu atoms are described by an Ar/3d¹⁰ effective core potential [31,32] and only Cu 4sp electrons are explicitly included in the substrate wave function. While the overall adsorbate geometry resulting from this restricted treatment is found quite similar compared to the full calculations the numerical results for interaction energies D are somewhat different. In the restricted calculations the positive D values at the Hartree–Fock level are increased by about 0.3 eV due to the missing Cu 3d orbital participation in the local adsorbate–substrate bond formation. The respective increase in D from the correlated calculations amounts to about 0.4 eV. This shows that the involvement of Cu 3d electrons in the local bond formation process at the surface is of moderate size concerning binding energetics and Cu 3d correlation contributions are small (about 0.1 eV) compared to those of Cu 4sp (about 0.8 eV). However, it should be noted that Cu 3d participation is essential for a correct binding energy balance in the present cluster since its neglect leads to positive rather than negative D values at the CI level.

In the present cluster system where the interaction energy D assumes rather small values contributions due to basis set superposition errors (BSSE) may become important and have to be considered. Detailed test calculations on the $\text{Cu}_7(4, 3)\text{C}_2\text{H}_2$ cluster and its subsystems, Cu_7 and C_2H_2 , based on the counterpoise method [27] show that BSSE corrections do contribute to the total interaction energy but do not affect the qualitative conclusions. The total energy of (distorted) C_2H_2 evaluated with the Cu_7 basis set included at the full equilibrium geometry of $\text{Cu}_7(4, 3)\text{C}_2\text{H}_2$, see Table 1a, is lower by 0.089 eV

compared to the calculation without the Cu_7 basis set. Analogously, the presence of the C_2H_2 basis set at equilibrium geometry lowers the total energy of Cu_7 by 0.037 eV. Altogether, these corrections result in a BSSE contribution of 0.125 eV which increases the computed D values of Table 1a, respectively yielding $D = +0.89$ eV at the Hartree–Fock and $D = -0.15$ eV at the CI level. Thus, the BSSE does not affect the qualitative energy results as stated before.

The computed equilibrium geometry of $\text{Cu}_7(4, 3)\text{C}_2\text{H}_2$ may be compared with experimental results for the $\text{C}_2\text{H}_2/\text{Cu}(111)$ adsorbate system [13] and with theoretical data for smaller surface clusters published previously. The equilibrium distance of C_2H_2 perpendicular to the Cu surface, $z_{\text{min}} = 3.18$ bohr, found in the present calculations is larger by 15% compared to the experimental value obtained from photoelectron diffraction (PED) on the real $\text{C}_2\text{H}_2/\text{Cu}(111)$ adsorbate system [13], $z_{\text{min}} = 2.66 \pm 0.11$ bohr (1.41 ± 0.06 Å). It is, however, closer to experiment and considerably smaller than the value, $z = 3.59$ bohr (1.9 Å), assumed in previous Hartree–Fock–Slater–LCAO studies on $\text{Cu}_n\text{C}_2\text{H}_2$, $n = 1-3$, clusters [18]. The rather large z_{min} value of the present calculations reflects to a major extent the quality of the surface representation by the small finite substrate cluster. In contrast, the increased C–C equilibrium distance, $d_{\text{C–C}} = 2.58$ bohr, found for $\text{Cu}_7(4, 3)\text{C}_2\text{H}_2$ is close to the experimental PED result for $\text{C}_2\text{H}_2/\text{Cu}(111)$ [13] yielding 2.80 ± 0.2 bohr (1.48 ± 0.10 Å) and is somewhat larger than the value (2.4 bohr) assumed in a previous cluster study [18]. Finally, the C–C–H bending angle of the adsorbate, $\theta = 60^\circ$ from the present model calculation, cannot be compared with PED data for $\text{C}_2\text{H}_2/\text{Cu}(111)$ since hydrogen positions cannot be observed in PED due to their small scattering cross section [13]. The computed angle is considerably larger than the value ($\theta = 30^\circ$) used in previous calculations [18].

The geometric and energetic results from the present calculations suggest for the $\text{C}_2\text{H}_2/\text{Cu}(111)$ system a competitive binding scheme. The adsorbate–substrate interaction energy D can be subdivided conceptually into contributions from two effects, (a) the geometric rearrangement of the C_2H_2 molecule by the adsorption which requires energy, and (b) the

binding of the distorted molecule near the substrate surface which gains energy. Both contributions must be of similar magnitude with (b) being slightly larger than (a) such that the adsorbate interacts overall weakly with the surface. The size of the two contributions can be estimated roughly from extended calculations on the free C_2H_2 molecule.

Fig. 2 shows potential hypersurfaces $E_{\text{tot}}(d_{C-C}, \theta)$ of the two lowest states of free C_2H_2 , $^1A'$ and $^3A'$, calculated in Hartree–Fock approximation where coordinates d_{C-C} refer to the C–C distance and θ to the C–C–H bending angle. Here the energy zero coincides with the total energy value of the $^1A'$ ground state at equilibrium. The calculations yield a difference in the total energy between the $^1A'$ equilibrium geometry ($d_{C-C} = 2.27$ bohr, $\theta = 0^\circ$) and that of the adsorbate ($d_{C-C} = 2.58$ bohr, $\theta = 60^\circ$) of 3.93 eV at the Hartree–Fock level and of 2.37 eV at the CI level. Further, the intersection of the $^1A'$ and $^3A'$ hypersurfaces which defines an energy barrier for concerted d_{C-C} and θ increases lies at about 3 eV. Test calculations show that this barrier can be lowered to 1.5 eV due to correlation contributions. So the present calculations suggest that an energy of

1.0–1.5 eV is required to change the C_2H_2 geometry from the free molecule situation to that necessary to stabilize C_2H_2 near the Cu substrate. This relatively large energy must be compensated by surface bond formation of the distorted C_2H_2 molecule.

An inspection of the molecular valence orbitals of linear and bent C_2H_2 can help to identify the nature of the local bond formation near the Cu surface. Fig. 3 shows contour plots of the highest occupied orbital $6a'$ (HOMO: $1\pi_u$ in $D_{\infty h}$ symmetry of linear C_2H_2 ; $4a_1$ in C_{2v} symmetry of bent C_2H_2) and of the lowest unoccupied orbital $7a'$ (LUMO: $1\pi_g$ in $D_{\infty h}$ symmetry of linear C_2H_2 ; $5a_1$ in C_{2v} symmetry of bent C_2H_2) along a plane containing all atom centers of the molecule. In linear C_2H_2 the HOMO (top left plot) is described by a bonding combination of C 2p functions at the two C centers and contributes to the C–C triple bond in acetylene. If the CH ends on both sides of the molecule are bent by 60° and the C–C distance increased to reflect the C_2H_2 adsorbate geometry the HOMO (bottom left plot) admixes C 2sp character such that its lobes at the C centers become asymmetric sticking out in a lone pair type fashion at the side adjacent to the Cu substrate. In

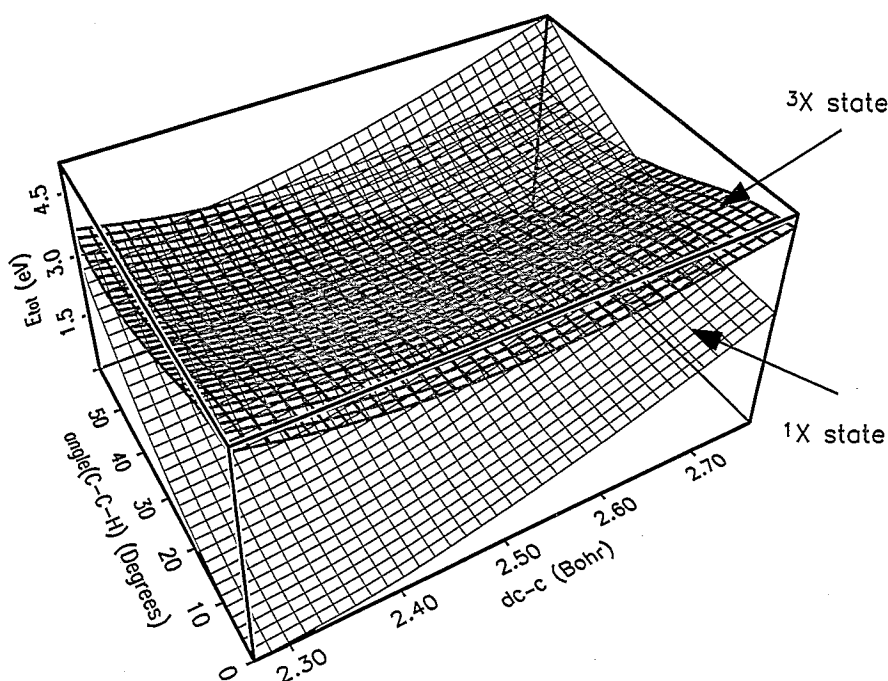


Fig. 2. Potential hypersurfaces of the lowest singlet and triplet states of free C_2H_2 , $^1A'$ and $^3A'$, calculated within the Hartree–Fock approach.

fact, this HOMO can be viewed as the origin of two lone pair orbitals which are located at the C ends of each of the CH subunits composing C_2H_2 and which are responsible of the high reactivity of the free CH radicals. As a result, the HOMO of the adsorbing C_2H_2 can easily hybridize with Cu 3d and 4sp orbitals resulting in a charge transfer (donation) from the adsorbate to the substrate. This charge transfer is partially compensated by a back-donation effect where Cu 3d and 4sp admix contributions of the adsorbate LUMO thereby transferring charge from the metal to the substrate. The LUMO which is described in the free C_2H_2 as an anti-bonding combination of C 2p functions (top right plot of Fig. 3) is modified in the adsorbate geometry by additional C 2sp contributions (bottom right plot) which increase its charge at the side adjacent to the Cu substrate and enhance its availability for back-donation. This donation/back-donation mechanism is well known from

the theory of metal complex [21] and surface bond formation [2,4]. Its significance for the metal–hydrocarbon binding is recognized as the Dewar–Chatt–Duncanson scheme [19,20] and has been pointed out in previous cluster studies [15–18]. Based on the energy balance described above the strength of the local bond formed between the (distorted) C_2H_2 adsorbate and the Cu surface is estimated to be of the order 1.0–1.5 eV.

The asymmetry of the C_2H_2 HOMO in the adsorbate geometry as well as its hybridization with substrate orbitals results in an effective weakening of the C–C bond which is further weakened by the partial occupation of the anti-bonding LUMO as a result of the back-donation effect at the surface. Altogether, the C–C bond order in C_2H_2 is expected to decrease near the surface. This is consistent with the increased C–C distance found for the adsorbate. Using typical C–C bond lengths from organic chem-

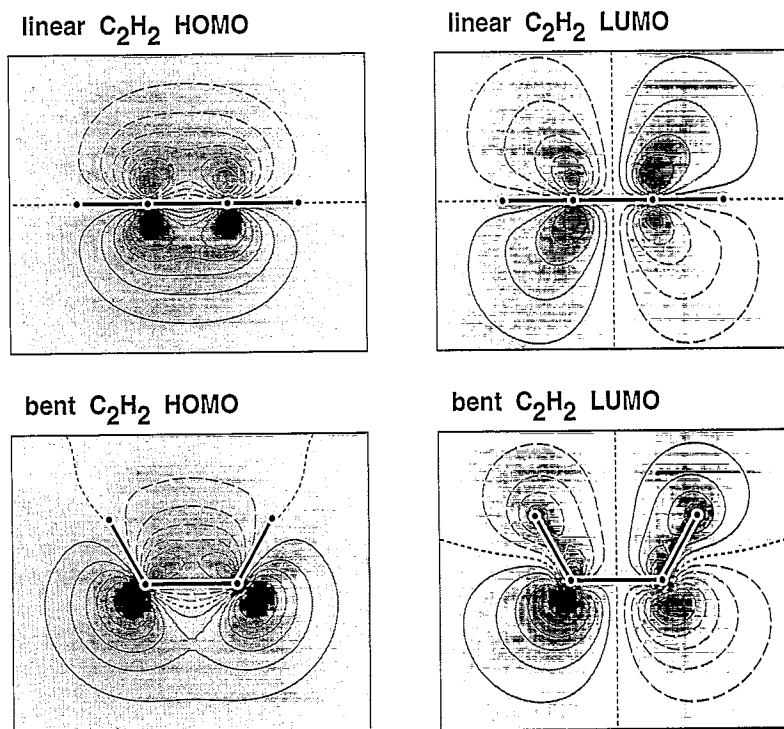


Fig. 3. Shaded contour plots of the highest occupied orbital (HOMO), $6a'$ ($1\pi_u'$, $4a_1$), and of the lowest unoccupied orbital (LUMO), $7a'$ ($1\pi_g'$, $5a_1$) of C_2H_2 in its free molecule (linear) and adsorbate (bent) geometry. The contour plane contains all atom centers of the molecule (marked by dots). Full (dashed) lines refer to positive (negative) wave function values with contours ranging from -0.28 a.u. to $+0.28$ a.u. with equidistant increments of 0.04 a.u. The shaded overlay sketches the orbital density.

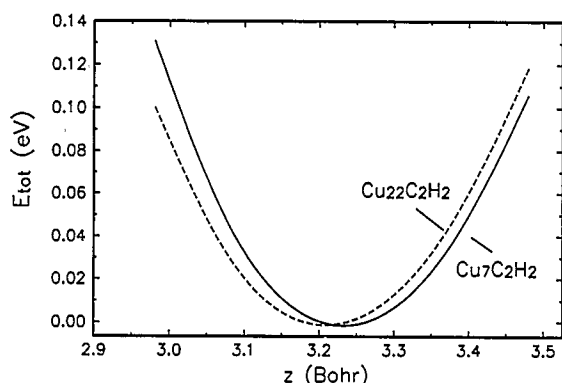


Fig. 4. Total energy curves $E_{\text{tot}}(z)$ for $\text{Cu}_7(4,3)\text{C}_2\text{H}_2$ and $\text{Cu}_{22}(12,7,3)\text{C}_2\text{H}_2$. The curves are given as a function of the perpendicular adsorbate–substrate distance z for a C–C separation $d_{\text{C-C}} = 2.77$ bohr and a C–C–H bending angle $\theta = 60^\circ$. Both curves are shifted rigidly such that the energy zero coincides with the respective minimum.

istry ($d_{\text{C-C}} = 2.27, 2.53$ and 2.91 bohr for triple, double and single bonds, respectively) the C–C distance from the present calculations suggests a C–C bonding with a bond order smaller than but close to two.

The binding mechanism discussed above has to be substantiated by systematic cluster studies including a set of substrate clusters differing in size and shape [22–24] to become fully convincing for the real $\text{C}_2\text{H}_2/\text{Cu}(111)$ surface system. While detailed calculations are still under way [33] preliminary Hartree–Fock results on the $\text{Cu}_{22}(12,7,3)\text{C}_2\text{H}_2$ cluster, see Fig. 1, confirm the qualitative picture of competitive binding. Further, the adsorbate binding curves turn out to be rather close between $\text{Cu}_7\text{C}_2\text{H}_2$ and $\text{Cu}_{22}\text{C}_2\text{H}_2$. This is illustrated in Fig. 4 which compares total energy curves for the two clusters. Here $E_{\text{tot}}(z)$ is shown as a function of the perpendicular adsorbate–substrate distance z for a C–C separation $d_{\text{C-C}} = 2.77$ bohr, reflecting the lateral distance between the fcc and hcp hollow sites at the $\text{Cu}(111)$ surface, and a C–C–H bending angle $\theta = 60^\circ$. Both curves have been shifted rigidly such that the energy zero coincides with the respective minimum. Obviously, the equilibrium distances z_{min} and the curvatures about the energy minima are rather similar.

4. Conclusions

The present cluster study on $\text{Cu}_7\text{C}_2\text{H}_2$ shows interesting geometric and energetic aspects of surface bond formation in the $\text{C}_2\text{H}_2/\text{Cu}(111)$ adsorbate system. The calculations confirm that C_2H_2 interacts rather weakly with the Cu substrate. Cluster values of the interaction energies amount to $D \approx 0.15$ eV. Further, the adsorbate geometry found for the $\text{Cu}_7\text{C}_2\text{H}_2$ cluster reflects the experimental geometry of the $\text{C}_2\text{H}_2/\text{Cu}(111)$ adsorbate system as observed in photoelectron diffraction [13]: C_2H_2 stabilizes in the cluster over the bridge site with its C–C axis parallel to the surface and the two C centers pointing towards adjacent 3-fold fcc and hcp hollow sites, the C–C distance of the adsorbate is greatly increased with respect to that of free C_2H_2 . Moreover, the calculations predict that both CH ends of adsorbed C_2H_2 are bent by about 60° pointing away from the surface which has not been observed so far and is larger than theoretical values published previously [18].

An analysis of the (small) C_2H_2 –Cu interaction energy D in the cluster identifies two competing contributions of comparable size. First, energy is required to restructure the free molecule transforming from its linear to a bent geometry with increased C–C distance. This energy is estimated to be 1.0–1.5 eV from the present calculations. Second, energy is gained as a result of local bond formation of the restructured C_2H_2 with the $\text{Cu}(111)$ surface atoms. The present calculations suggest that a major part of this surface bond is due to a Dewar–Chatt–Duncanson [19,20]-type donation/back-donation mechanism involving the $6a'$ HOMO and $7a'$ LUMO of adsorbed C_2H_2 and Cu 3d as well as 4sp orbitals. While this mechanism has been proposed qualitatively in earlier cluster studies on the $\text{C}_2\text{H}_2/\text{metal}$ adsorbate system [15–18] the present work gives an estimate of 1.0–1.5 eV for the energy connected with this bond formation. Further, we find that in the present system where the adsorbate–substrate interaction consists of two competing contributions of about equal size resulting in a small net effect electron correlation becomes important for a correct evaluation of the energy balance. In fact, the calculations yield C_2H_2 to stabilize globally at the Cu surface ($D < 0$) only after valence electron correlation is included.

Clearly, the present model study needs to be extended to larger clusters [33] including more complex geometry variations of the adsorbate in order to give fully convincing account of the adsorbate behavior at the surface. In particular, the present calculations cannot describe the dynamics of the adsorption process which involve concerted adsorbate geometry variations and possible reaction barriers along the adsorption path. However, this study suggests that the $C_2H_2/Cu(111)$ adsorbate system is an interesting example of a surface interaction determined by competitive effects which may apply also to other hydrocarbon adsorbate systems. As a possible candidate we mention benzene adsorption on metal surfaces where recent DLEED investigations on $C_6H_6/Pt(111)$ [34] indicate weak adsorbate bonding connected with noticeable changes in the C–C distances.

Acknowledgements

The authors are grateful for valuable discussions with A.M. Bradshaw. This work was funded in part by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie, Frankfurt. Further support was based on grant No. 3T09A from the State Committee for Scientific Research of Poland.

References

- [1] See e.g.: Surface Science and Catalysis, Vol. 45, Eds. B. Delmon and J.T. Yates (Elsevier, Amsterdam, 1989).
- [2] G.A. Somorjai, Introduction to Surface Chemistry and Catalysis (Wiley, New York, 1994).
- [3] A. Bielanski and J. Haber, Oxygen in Catalysis, Vol. 43 of Chemical Industries Series (Marcel Dekker, New York, 1991).
- [4] See e.g.: M.C. Desjonquères and D. Spanjaard, Concepts in Surface Science, Vol. 30 of Springer Series in Surface Sciences (Springer, New York, 1993).
- [5] K. Hermann, K. Freihube, T. Greber, A. Böttcher, R. Grobecker, D. Fick, and G. Ertl, Surf. Sci. 313 (1994) L806.
- [6] T. Greber, K. Freihube, R. Grobecker, A. Böttcher, K. Hermann, G. Ertl and D. Fick, Phys. Rev. B 50 (1994) 8755.
- [7] K. Freihube, PhD thesis, Freie Universität Berlin, 1994.
- [8] K. Hermann and P.S. Bagus, Phys. Rev. B 17 (1978) 4082.
- [9] K. Hermann and P.S. Bagus, Phys. Rev. B 20 (1979) 1603.
- [10] K. Hermann and P.S. Bagus, Phys. Rev. B 16 (1977) 4195.
- [11] K. Hermann, P.S. Bagus and C.J. Nelin, Phys. Rev. B 35 (1987) 9467.
- [12] J. Küppers, F. Nitschke, K. Wandelt and G. Ertl, Surf. Sci. 87 (1979) 295.
- [13] S. Bao, K.-M. Schindler, P. Hofmann, V. Fritzsche, A.M. Bradshaw and D.P. Woodruff, Surf. Sci. 291 (1994) 295.
- [14] S. Bao, P. Hofmann, K.-M. Schindler, V. Fritzsche, A.M. Bradshaw, D.P. Woodruff and M.C. Asensio, J. Phys.: Condens. Matter 6 (1994) L93.
- [15] A.B. Anderson, J. Am. Chem. Soc. 99 (1977) 696.
- [16] T.N. Rhodin, C.F. Brucker and A.B. Anderson, J. Phys. Chem. 82 (1978) 894.
- [17] P. Geurts and A. van der Avoird, Surf. Sci. 102 (1981) 185.
- [18] P. Geurts and A. van der Avoird, Surf. Sci. 103 (1981) 416.
- [19] M.J.S. Dewar, Bull. Soc. Chim. Fr. 18 (1951) C79.
- [20] J. Chatt and L.A. Duncanson, J. Chem. Soc. (1953) 2939.
- [21] M.R. Albert and J.T. Yates, The Surface Scientist's Guide to Organometallic Chemistry (ACS, Washington, 1987).
- [22] K. Hermann, M. Witko, L.G.M. Pettersson and P. Siegbahn, J. Chem. Phys. 99 (1993) 610.
- [23] M. Witko and K. Hermann, J. Chem. Phys. 101 (1994) 10173.
- [24] M. Witko, K. Hermann, D. Ricken, W. Stenzel, H. Conrad and A.M. Bradshaw, Chem. Phys. 177 (1993) 363.
- [25] For the present calculations the STOCKHOLM program system was used to obtain Hartree–Fock and correlated (CI, MCPD) wave functions. STOCKHOLM is a general purpose quantum chemical set of programs written by P.E.M. Siegbahn, M.R.A. Blomberg, L.G.M. Pettersson, B.O. Roos and J. Almlöf.
- [26] D.P. Chong and S.R. Langhoff, J. Chem. Phys. 84 (1986) 5606.
- [27] S.F. Boys and F. Bernardi, Mol. Phys. 19 (1970) 553.
- [28] F.B. Van Duijneveldt, IBM Research Report No. RJ 945, 1971.
- [29] C.W. Bauschlicher, P.S. Bagus and H.F. Schaefer III, IBM J. Res. Dev. 22 (1978) 213.
- [30] H. Tatewaki and S. Huzinaga, J. Chem. Phys. 71 (1979) 4339.
- [31] H. Åkeby, I. Panas, L.G.M. Pettersson, P.E.M. Siegbahn and U. Wahlgren, J. Phys. Chem. 94 (1990) 5471.
- [32] I. Panas, P.E.M. Siegbahn and U. Wahlgren, Chem. Phys. 12 (1987) 325.
- [33] K. Hermann and M. Witko, to be published.
- [34] A. Wander, G. Held, R.Q. Hwang, G.S. Blackman, M.L. Xu, P. de Andres, M.A. Van Hove and G.A. Somorjai, Surf. Sci. 249 (1991) 21.