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HARTREE–FOCK–SLATER–LCAO STUDIES OF THE ACETYLENE–TRANSITION METAL INTERACTION
IV. Dissociation fragments on Ni surfaces; cluster models

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Using the Hartree–Fock–Slater–LCAO method we have calculated the ionization energies for the acetylene fragments CH, CH_2 and C_2H adsorbed on small Ni clusters and we have compared these with the UPS spectrum measured for dissociatively adsorbed C_2H_2 on the Ni(111) surface. For none of these fragments the calculated spectrum is in one-to-one correspondence with the experimental one. Although one should perform further, more extensive, calculations in order to be conclusive, we suggest as a possible explanation of this discrepancy that other (low intensity or strongly broadened) peaks might be hidden in the experimental spectrum. If such peaks would be found, our results can be used to identify the adsorbed fragments since the spectra calculated for the different species are rather different. On the other hand, we conclude that these spectra do not depend sensitively on the adsorption site or on the position of the adsorbed fragments.

1. Introduction

In the previous papers I and II [1,2] in this series we have studied the molecular adsorption of acetylene on Ni, Fe and Cu surfaces. This was done by means of Hartree–Fock–Slater (HFS)–LCAO calculations on C_2H_2 interacting with small metal clusters which model different adsorption sites on the transition metal low index planes and comparison of the calculated properties with experimental (spectroscopic) data. A comparison has been made also (in paper III [3]) with C_2H_2 binding to mono- and dinuclear nickel complexes with carbonyl and isocyanide ligands. In catalytic processes involving hydrocarbons bond breaking by the (transition metal) catalyst is an important step. For C_2H_2 adsorbed on the low index planes of Fe [4–7] and Ni [8–10] such bond breaking has been found experimentally at somewhat higher temperatures and coverages, compared with the molecularly adsorbed state. In order to study the various possible reaction pathways one must identify the dissociation fragments, but this identification is not so easy. Much work has been done, for instance, on the dissociative adsorption of

C_2H_2 on the Pt(111) surface but three different structures have been suggested, CH_3–CH [11,12], CH_3–C [13,14] and CH_2=C [12,14,15], for what is probably the same species. From ultraviolet photoelectron spectroscopy (UPS), temperature programmed desorption (TPD) and low energy electron diffraction (LEED) [8] and from electron energy loss spectroscopy (ELS) [9,10] it has been concluded that on Ni(111) C_2H_2 dissociates into CH species, at $T \simeq 300$ to 400 K; in paper I we have found indications for a considerable C–C bond weakening, by the interaction with the Ni surface, which must precede this dissociation. At still higher temperatures $T \gtrsim 450$ K, CH_2 fragments seem to occur [9]. Also on Fe(100) and Fe(111) surfaces CH, CH_2 and other species have been suggested [4–7].

In the present paper we study three possible dissociation products of acetylene, CH, CH_2 and C_2H, adsorbed on nickel surfaces at different sites, represented by small clusters of Ni atoms (1, 2 or 3 atoms). The non-empirical MO method used is the same as in our previous work [1–3], i.e. the HFS–LCAO method. We try to characterize the adsorbed fragments by comparing the calculated ionization energies for the different species at different sites with the UPS spectrum measured for dissociated C_2H_2 on Ni(111) at $T \simeq 300$ to 400 K [8]. Other theoretical studies which have been performed on models for adsorbed hydrocarbon fragments are semi-empirical extended Hückel calculations of these fragments interacting with Fe, Ni and Pt clusters [16–20] and ab initio Hartree–Fock–LCAO (and GVB and CI) calculations of the fragments binding to a single metal atom, Mn [21], Ni [22–24] or Li [15].

2. Method and calculations

As in paper I, we have used the self-consistent spin-restricted HFS–LCAO method in its core pseudopotential version [25–28]. Also the atomic orbital basis (double zeta Slater type orbitals [29]) and electron density fit functions (s-, p-, d-, f- and g-type) have been chosen as in I: 3d, 4s and 4p orbitals on Ni (from the $3d^8 4s^2\ {}^3F$ state), 2s and 2p on C and 1s on H.

The metal–CH clusters studied are NiCH (linear, $C_{\infty v}$), Ni_2CH (with CH perpendicular to the Ni–Ni axis, C_{2v}) and Ni_3CH (CH perpendicular to the Ni_3 plane, C_{3v}). For CH_2 adsorption we have considered $NiCH_2$ (planar, C_{2v}) and Ni_2CH_2 (the CH_2 plane perpendicular to the Ni–Ni axis, C_{2v}). These clusters model different adsorption sites (on top, bridged, threefold) occurring on the Ni(111) surface (and some of them on other surfaces too). The CH and CH_2 fragments are placed with the carbon atom closest to the metal atoms and all Ni–C distances equal to 1.90 Å (the same as the Ni–C distance in the nickel–C_2H_2 clusters in paper I); for Ni_3CH we have also performed a calculation with shorter Ni–C distance: 1.69 Å. The C–H distance in the Ni_nCH clusters equals 1.06 Å (the acetylenic value [30]); in the Ni_nCH_2 clusters it is 1.09 Å, while the HCH angle is 120° (these values are averages from the experimental singlet and triplet CH_2 structures [31–34]). The structure of the Ni_3C_2H cluster (C_s symmetry) is taken from the similar inorganic complexes [π-$(C_5H_5)Fe_3(CO)_7C_2C_6H_5$] [35] and [$Ru_3(CO)_9H\{C_2C(CH_3)_3\}$] [36]. The plane of the bent C_2H fragment, CCH angle 135° with the H atom pointing away from the Ni_3 plane, is perpendicular to this Ni_3 plane and contains one Ni atom (Ni_γ), while it bisects the Ni–Ni axis of the other two metal atoms (Ni_α–Ni_β). The C–C axis makes an angle of 10.5° with the Ni_3 plane (the C atom closest to the "surface" is denoted as C_α; the other one, which bears the H atom, is labelled C_β). The following distances have been chosen: Ni_γ–C_α: 1.83 Å, Ni_γ–C_β: 2.98 Å, $Ni_{\alpha,\beta}$–$C_{\alpha,\beta}$: 2.04 Å, C_α–C_β: 1.30 Å, C_β–H: 1.06 Å. This model corresponds with threefold bonding of the C_2H species to the surface: the C_α atom forms a single σ-type bond with Ni_γ, the (acetylenic) π-orbitals in C_2H are involved in μ_2-type bonding with the Ni_α and Ni_β atoms (cf. paper I). In all clusters (with more than one Ni atom) the Ni–Ni distances are taken equal to the metal nearest neighbour value: 2.49 Å [30].

The ionization energies, which are compared with the experimental UPS spectrum, have been calculated by the HFS method, mostly in the transition state formalism [26,37]. Since the relaxation shifts for the valence levels of the adsorbed fragments appear to be almost uniform (see section 3, cf. papers I and II also) ground state calculations of the level splittings give practically the same picture.

3. Results

The measured UPS spectrum of dissociated C_2H_2 species (at $T \simeq 300$ to 400 K) on the Ni(111) surface shows peaks at −15.2 and −7.3 to −8 eV, relative to the work function [8]. It is possible that the −7.3 to −8 eV peak corresponds with (at least) two ionization levels which are not well resolved. Since it is hard to predict accurately the absolute ionization energies and the work function for metal–adsorbate systems (although the HFS–LCAO results on small cluster models with C_2H_2 are reasonably good, cf. paper I), we look at the level splittings. (It would be even better to look at the changes in these splittings caused by adsorption, as we have done for molecular C_2H_2, but the UPS spectra for the unadsorbed acetylene fragments are not known experimentally.) So the experimental data to be explained by the calculations are a gap of about 7.5 eV between two ionized levels and possibly a splitting of the highest level of about 0.7 eV.

3.1 Nickel–CH

The free CH radical possesses three (partially) occupied orbitals: two of σ type, 1σ which is mainly C(2s) and 2σ which is C–H bonding, and one (doubly degenerate) π orbital. In table 1 we have summarized the relative positions of the levels of mainly CH character in the nickel–CH clusters. In the Ni_2CH cluster the doubly degenerate π orbital is split (by ~1 eV); we have indicated the average position of

Table 1
Level splittings Δ (in eV) for nickel–CH clusters [a]

Ni–C (Å)	NiCH		Ni_2CH		Ni_3CH		
	1.90		1.90		1.90		1.69
	GS	TS	GS	TS	GS	TS	GS
$\Delta_{2\sigma-1\sigma}$	5.4	5.8	5.2	5.6	4.7	4.9	5.3
$\Delta_{\pi-1\sigma}$	8.8	9.8	8.5	9.2	8.0	8.7	8.1

[a] GS stands for ground state, TS for transition state results.

the two π levels. From this table we observe that the ground state (GS) and transition state (TS) calculations give essentially the same results (indicating a uniform relaxation shift). It is striking that the picture is not very different for the different adsorption sites (one, two or three atom clusters). The same insensitivity of the ionization spectrum with respect to the metal site has been found for molecularly adsorbed C_2H_2, cf. papers and II. Moreover, it has been concluded there, too, that extension of the small metal clusters by one or two extra atoms did hardly affect the calculated ionization energies; so we expect that the positions of the levels would not be significantly changed if we would enlarge the metal clusters. The calculated results do not seem to agree with the experimental data, however. We never find a gap nearly as wide as 7.5 eV between two peaks. Also a significant decrease of the Ni–C distance (from 1.90 to 1.69 Å) does not provoke this result. If we would assume that the 2σ peak has small intensity and is not well visible in the experimental UPS spectrum, the agreement between the experimental (7.5 eV) and the calculated ($\simeq$8.5 eV) splitting is reasonably good.

3.2. Nickel–CH_2

Free CH_2 (methylene) has four (partially) occupied orbitals: $1a_1$, $1b_2$, $2a_1$ and $1b_1$. In table 2 we present the relative positions of the levels in the nickel–CH_2

Table 2
Level splittings Δ (in eV) for nickel-CH_2 clusters [a]

	$NiCH_2$		Ni_2CH_2	
	GS	TS	GS	TS
$\Delta_{1b_2-1a_1}$	5.1	4.9	4.9	4.8
$\Delta_{2a_1-1a_1}$	7.5	7.5	6.2	6.6
$\Delta_{1b_1-1a_1}$	9.5	10.3	8.5	9.2

[a] GS stands for ground state, TS for transition state results.

clusters which have mainly the character of these CH_2 orbitals. Just as for CH the GS and TS results are essentially the same. Moreover, we observe also here that the two nickel sites (on top or twofold) yield almost the same ionization spectrum. Again we do not find agreement with the experimental spectrum; here it would be harder than in the case of CH to reconcile the results by using the argument of low intensity peaks since we have calculated more levels which are all localized on the CH_2 fragment and which have no counterpart in the experimental spectrum.

3.3. Nickel–C_2H

The occupied orbitals of C_2H resemble those of acetylene in their character: 3σ corresponds with $2\sigma_g$, 4σ with $2\sigma_u$, 5σ with $3\sigma_g$, 1π with $1\pi_u$. In our adsorption cluster, Ni_3C_2H with C_s symmetry, the following (valence) orbitals are essentially composed of these orbitals of the C_2H fragment: $3\sigma \rightarrow 1a'$, $4\sigma \rightarrow 2a'$, $5\sigma \rightarrow 3a'$, $1\pi_\perp \rightarrow 4a'$, $1\pi_{/\!/} \rightarrow 1a''$ (the lables $\perp$ and $/\!/$ denote π orbitals perpendicular and parallel to the "surface", respectively). Table 3 shows the relative positions of these levels. It also contains the positions of the acetylenic levels in the cluster μ_3-C_2H_2–Ni_3, which models the molecular adsorption of C_2H_2 on a threefold nickel (111) site. We observe some resemblance between the calculated spectra of the adsorbed C_2H fragment and molecularly adsorbed C_2H_2, but also there is a marked difference, viz. the higher energy of the $2a'$ (the acetylenic $3\sigma_g$) orbital. Again, we do not find the experimentally observed two peak structure with a gap of 7.5 eV. The $2a'$ level divides the gap between the lower $1a'$ peak and the higher (broadened) peak which might be assumed to contain the $3a'$, $4a'$ and $1a''$ levels. This $2a'$ level (corresponding with the acetylenic $3\sigma_u$ orbital) is mainly localized on the C–H bond, just as the 2σ level which divides the gap for the adsorbed CH fragment. The agreement with experiment is worse than for CH adsorption, however, even if we would assume the $2a'$ peak to have low intensity, since the gap between the remaining two peaks would be too large ($\simeq$9.7 eV).

Table 3
Level splittings Δ (in eV) for Ni_3C_2H and μ_3-C_2H_2–Ni_3

	Ni_3C_2H GS [a]		μ_3-C_2H_2–Ni_3 [b] $\angle_{CCH} = 150°$, GS [a]
$\Delta_{2a'-1a'}$	5.9	$\Delta_{2\sigma_u-2\sigma_g}$	5.8
$\Delta_{3a'-1a'}$	9.3	$\Delta_{3\sigma_g-2\sigma_g}$	6.9
$\Delta_{4a'-1a'}$	9.7	$\Delta_{\pi_{u\perp}-2\sigma_g}$	9.7
$\Delta_{1a''-1a'}$	10.1	$\Delta_{\pi_{u/\!/}-2\sigma_g}$	10.5

[a] GS stands for ground state results.
[b] From paper I [1].

4. Conclusions

Our calculations have yielded rather different ionization spectra for different acetylene fragments CH, CH_2 and C_2H adsorbed on nickel surface models, but none of these spectra is in one-to-one correspondence with the UPS spectrum measured for dissociated C_2H_2 on the Ni(111) surface. If we assume that this discrepancy is not caused by inaccuracies in the level positions calculated by the HFS method (the errors in these level positions are larger than the errors in the level shifts caused by adsorption, cf. paper I), the following explanations can be suggested. Our models, of course, could have the wrong geometry or they could be too small, but we have found that the calculated level positions are rather insensitive to the size and geometry of the cluster models. Also one might conclude that the occurring fragments are of different chemical composition, but we think it very unlikely that larger species such as CH_3–CH, CH_3–C or CH_2=C, which have been suggested to occur on Pt(111) surfaces, would yield the UPS spectrum observed for Ni(111). Such species have various chemical bonds with more or less localized molecular orbitals which we expect to yield ionization energies over the same energy range as the smaller species that we have studied with even smaller gaps. (And certainly not just the two peaks with a wide gap of 7.5 eV found in the experimental spectrum.) The most probable conjecture, to our opinion, is that one (or more) of the calculated ionization levels corresponds with a peak of lower intensity or one which is strongly broadened by coupling to the metal bands, so that it is not well visible in the experimental UPS spectrum. If we assume this to be the case, our results are not in conflict with the CH structure proposed for the dissociation fragments of C_2H_2 on Ni(111) [8–10]. In view of this discussion we recommend to look in the experimental UPS spectrum for weak bands (in the 7.5 eV gap?); or better, to make angularly resolved UPS measurements (as have been reported for CO on Ni(100) [38]) which would facilitate the assignment of the peaks by considering the different directional character of the orbitals in the adsorbed species. From the theoretical side, it would be very useful to calculate the intensities of the different ionization peaks, as it has been done for CO and N_2 [39] and for adsorbed O [40–42] and S [41].

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