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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$_2$H adsorbed on small Ni clusters and we have compared these with the UPS spectrum measured for dissociatively adsorbed C$_2$H$_2$ 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$_2$H$_2$ 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$_2$H$_2$ 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$_2$H$_2$ 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$_2$H$_2$ 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$_2$H$_2$ dissociates into CH species, at $T \approx 300$ 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 $T \geq 450$ 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$_2$H, 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$_2$H$_2$ on Ni(111) at $T \approx 300$ 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 Is on H.

The metal-CH clusters studied are NiCH (linear, C$_{\infty v}$), Ni$_2$CH (with CH perpendicular to the Ni-Ni axis, C$_{2v}$) and Ni$_3$CH (CH perpendicular to the Ni$_3$ plane, C$_{3v}$). For CH$_2$ adsorption we have considered NiCH$_2$ (planar, C$_{2v}$) and Ni$_2$CH$_2$ (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$_2$H$_2$ clusters in paper I); for Ni$_3$CH we have also performed a calculation with shorter Ni-C distance: 1.69 Å. The C-H distance in the Ni$_n$CH clusters equals 1.06 Å (the acetylenic value [30]); in the Ni$_n$CH$_2$ 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$_3$C$_2$H cluster (C$_s$ symmetry) is taken from the similar inorganic complexes [π(C$_3$H$_5$)Fe$_3$(CO)$_7$C$_2$C$_6$H$_5$] [35] and [Ru$_3$(CO)$_9$H$_2$C$_2$(CH$_3$)$_3$]$_3$ [36]. The plane of the bent C$_2$H 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$_7$), while it bisects the Ni—Ni axis of the other two metal atoms (Ni$_a$—Ni$_b$). 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$_a$; the other one, which bears the H atom, is labelled C$_b$). The following distances have been chosen: Ni$_7$—C$_a$: 1.83 Å, Ni$_7$—C$_b$: 2.98 Å, Ni$_a$—C$_b$: 2.04 Å, C$_a$—C$_b$: 1.30 Å, C$_b$—H: 1.06 Å. This model corresponds with threefold bonding of the C$_2$H species to the surface: the C$_a$ atom forms a single σ-type bond with Ni$_7$, the (acetylenic) π-orbitals in C$_2$H are involved in μ$_2$-type bonding with the Ni$_a$ and Ni$_b$ 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$_2$H$_2$ species (at $T \approx 300$ 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$_2$H$_2$ 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$_2$H$_2$, 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$_2$CH cluster the doubly degenerate π orbital is split (by ~1 eV); we have indicated the average position of
the two \( \pi \) 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 \( \text{C}_2\text{H}_2 \), cf. papers I 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 \( 2\sigma \) 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 (\( \approx 8.5 \) 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\(_2\)
clusters which have mainly the character of these CH₂ 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 CH₂ fragment and which have no counterpart in the experimental spectrum.

3.3. Nickel–C₂H

The occupied orbitals of C₂H resemble those of acetylene in their character: 3σ corresponds with 2σ₈, 4σ with 2σ₈, 5σ with 3σ₈, 1π with 1π₈. In our adsorption cluster, Ni₃C₂H with C₃v symmetry, the following (valence) orbitals are essentially composed of these orbitals of the C₂H fragment: 3σ → 1a', 4σ → 2a', 5σ → 3a', 1π₁ → 4a', 1π₈ → 1a'' (the labels 1 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 μ₃-C₂H₂–Ni₃, which models the molecular adsorption of C₂H₂ on a threefold nickel (111) site. We observe some resemblance between the calculated spectra of the adsorbed C₂H fragment and molecularly adsorbed C₂H₂, but also there is a marked difference, viz. the higher energy of the 2a' (the acetylenic 3σ₈) 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 3σ₈ 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 (∼9.7 eV).

| Table 3 |
| Level splittings Δ (in eV) for Ni₃C₂H and μ₃-C₂H₂–Ni₃ |
| Ni₃C₂H | μ₃-C₂H₂–Ni₃ \( L_{\text{CCH}} = 150° \), GS |
| GS a | GS a |
| Δ₂a'–1a' | 5.9 | Δ₂σ₈−2σ₈ | 5.8 |
| Δ₃a'–1a' | 9.3 | Δ₃σ₈−2σ₈ | 6.9 |
| Δ₄a'–1a' | 9.7 | Δ₄σ₈−2σ₈ | 9.7 |
| Δ₁a''–1a' | 10.1 | Δ₁π₈−2σ₈ | 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, CH₂ and C₂H adsorbed on nickel surface models, but none of these spectra is in one-to-one correspondence with the UPS spectrum measured for dissociated C₂H₂ 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 CH₃—CH, CH₃—C or CH₂=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 C₂H₂ 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 N₂ [39] and for adsorbed O [40—42] and S [41].

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