Bonding of Ethylene to Diatomic Nickel according to a Self-Consistent-Field, $X\alpha$, Scattered-Wave Model*

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The electronic structure of a model "surface complex" consisting of a Ni diatom and an ethylene molecule has been calculated using the self-consistent-field, $X\alpha$, scattered-wave method. Comparison of calculated π-orbital bonding shifts with recent photoemission spectra for chemisorption of ethylene on nickel favors a π-bonded complex over a di-σ-adsorbed complex. Charge distributions of various molecular orbitals indicate that the C-C double bond is weakened more for the latter molecular arrangement, suggesting such a complex as a likely intermediate in heterogeneous reactions.

Reliable microscopic information on the interaction of transition metals with unsaturated hydrocarbons is becoming available.[1,2] Photoemission studies of acetylene, ethylene, and benzene chemisorbed on a Ni(111) surface have yielded the first direct observation of π-d bonding.[1] Ussing the self-consistent-field (SCF), $X\alpha$, scattered-wave (SW) method,[3] a reasonably accurate calculation of the electronic structure of Zeise's anion and especially of the Pt-ethylene bond has been given recently.[4] We report here the first $X\alpha$-SW calculations for a Ni-ethylene "surface complex."[5] They were undertaken in order to provide an additional test for the local-bonding approach to chemisorption,[6] to gain further information on the electronic structure of a chemisorbed ethylene molecule, and to possibly extract information from the photoemission spectrum on the geometry of the "surface complex."

It is commonly accepted[7,8] that ethylene (C_2H_4) binds to transition metals through an interaction of its π electrons with the metal d electrons. However the geometry of the chemisorbed ethylene (neglecting for the moment possible dehydrogenation, etc., after chemisorption) relative to the surface atoms is controversial. One assumption is that ethylene forms a π complex coordinating symmetrically to a single metal atom, as suggested by Dewar[7,8] and found in many organometallic complexes. From various surface reactions[9,10] and from infrared spectra of ethylene chemisorbed on silica-supported Ni,[11] it has been concluded, however, that each of the two carbon atoms forms a σ bond to a different metal atom.

As a model for the "surface complex" we choose a Ni diatom with a bond length of 2.492 Å (4.709 a.u.) equal to the nearest-neighbor distances in bulk Ni, and an ethylene molecule with equilibrium geometry. Corresponding to the two possible bonding schemes, two different geometrical arrangements have been studied. In the complex representing the di-σ-adsorbed ethylene, the Ni-Ni bond has been taken parallel to the plane of the ethylene molecule; in the π complex the Ni-Ni bond was arranged perpendicular to that plane and symmetric to the C-C bond. Both model complexes exhibit C_{2v} symmetry.

The distance of chemisorbed ethylene to the metal surface is unknown. Guided by the sum of covalent radii and by distances found in x-ray (1.9-2.2 Å) crystallographic studies of Ni-olefin complexes, a value of 2.0 Å was chosen for the distance between the two parallel bonds in the di-σ complex and for the distance from the bonding Ni atom to the center of the C-C bond in the π complex. (According to previous $X\alpha$ calculations the results should not be sensitive to small changes in this distance.) The radii of the muffin-tin spheres surrounding the various Ni atoms were chosen as half the Ni-Ni bond length. For ethylene we have used the overlapping-sphere parametrization[12] (parameter set D of Ref. 12). The size of the outer sphere was kept minimal in both cases (di-σ complex, $r_{\text{out}} = 4.828$ a.u.; π complex, $r_{\text{out}} = 6.283$ a.u.). The atomic exchange parameters α for carbon and hydrogen were taken from spin-polarized atomic calculations[12]; the α value for nickel was taken from the tabulation by Schwarz.[13] The α values for the interatomic and the extramolecular regions were set equal and taken as the weighted average over the atomic α values, where ethylene was given the same weight as one Ni atom.[4] The core charges corresponding to the configurations C s^2 and Ni $1s^22p^6$ as determined from atomic calculations were included but kept fixed during the SCF cycles.[4] The remaining 48 electrons were fully taken into account in the iterations to self-consistency according to

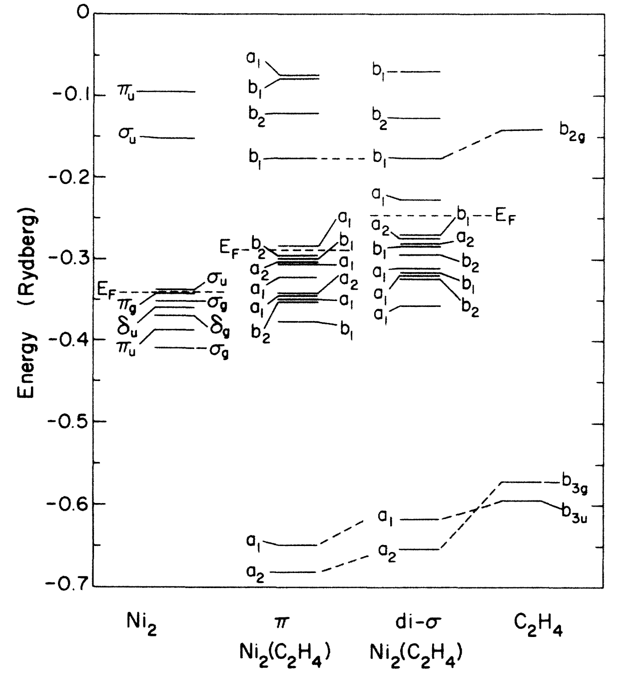

FIG. 1. SCF-$X\alpha$-SW electronic energy levels for the model complex Ni_2-C_2H_4: π complex and di-σ complex. Also shown are the $X\alpha$-SW levels of Ni_2 and C_2H_4. The levels are filled up to the Fermi level E_F, marked by a dashed line. Other levels (not shown) are not involved in the metal-ethylene binding.

the usual $X\alpha$-SW procedure.[3,4]

The resulting $X\alpha$-SW ground-state orbital energies for the two geometries are compared in Fig. 1. Only low-lying unoccupied orbitals and the valence-type orbitals with energies above -0.7 Ry are shown. The levels are labeled according to the irreducible representations of the point group C_{2v} and filled as marked up to the Fermi level, E_F. Also shown in Fig. 1 are the $X\alpha$-SW energy levels of Ni_2[14] and C_2H_4[12] which fall in the displayed range; for ethylene these are the π and π* levels b_{3u} and b_{2g}, respectively, and the highest σ level b_{3g}. To discuss and compare the bonding in the two model complexes we make use of the orbital charge distributions as obtained from the SCF-$X\alpha$-SW calculations, as well as of contour plots of the individual orbitals (some typical ones are indicated in Figs. 2 and 3). Thereby a clear assignment of the levels to the two components of each model complex is possible. The levels between -0.3 and -0.4 Ry correspond to the Ni diatom and represent the Ni d band. They undergo some mixing and a slight upward shift due to the interaction with the ethylene. This parallels a reduction of the Ni work function,

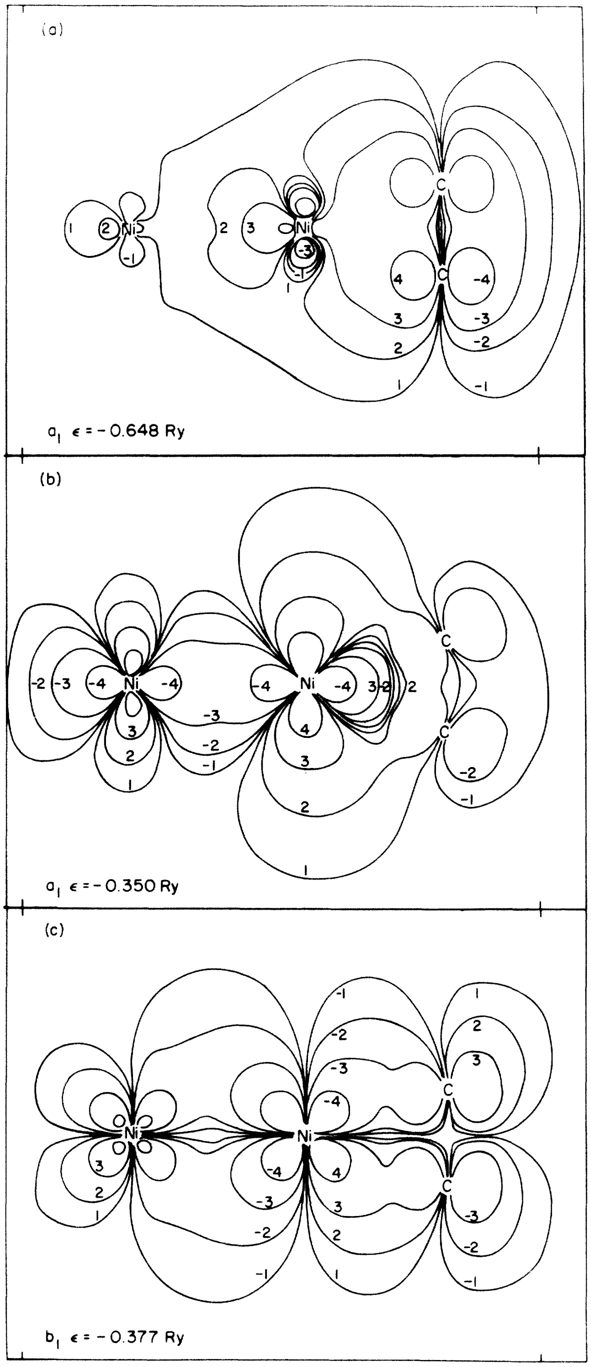

FIG. 2. Contour plots for individual bonding orbitals of the π complex. The contour values increase in absolute magnitude with increasing absolute values of the contour labels. The sign of the labels gives the sign of the orbital lobes. The selected set of the contour values plotted is the same for each of the three orbitals. (a) The ethylene π orbital, (b) the a_1 orbital giving the main contribution to the Ni-Ni bond, (c) the b_1 orbital showing significant π* backbonding.

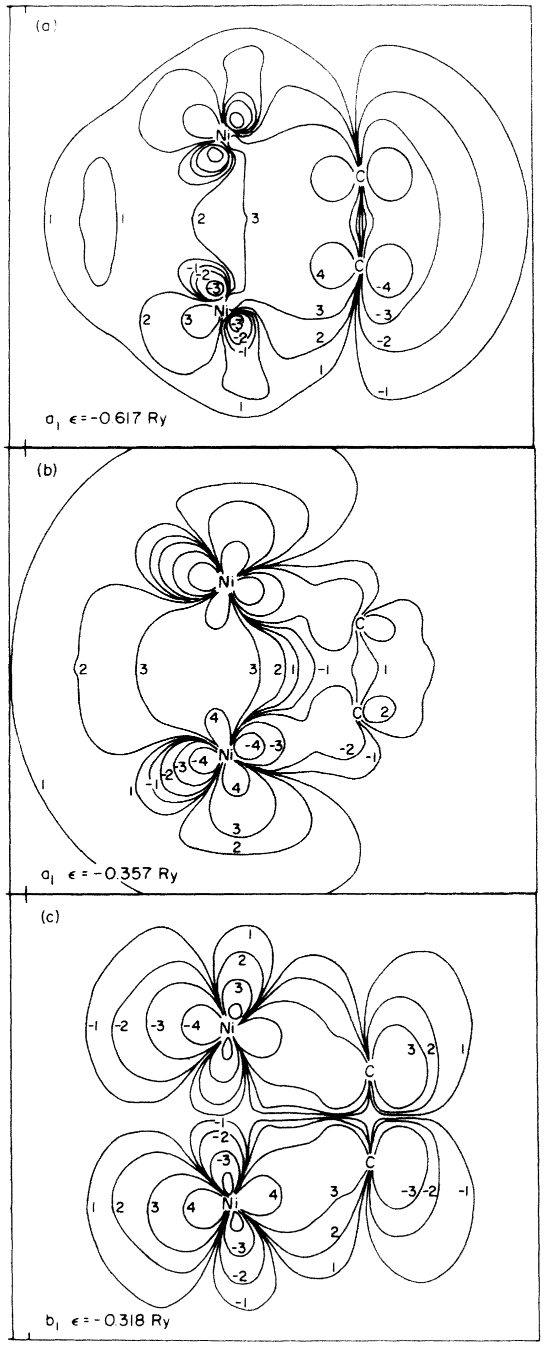

FIG. 3. Contour plots for orbitals of the di-σ complex. The orbitals shown correspond to those of Fig. 2. The contour values are the same.

$\Delta\varphi = -0.9$ eV, found after chemisorption of ethylene.[1] Taking the differences of the highest occupied $X\alpha$-SW orbital energies in each model complex and Ni_2, we find $\Delta\varphi_\pi = -0.60$ eV in the π complex and $\Delta\varphi_\sigma = -0.90$ eV in the di-σ complex.

The ethylene remains mostly unchanged in both complexes as can be inferred from the charge distributions of the corresponding orbitals. This is consistent with experimental information,[9,11] especially with the structure of the photoemission peaks corresponding to σ levels.[1] The only level found to interact strongly is the π level b_{3u}, again consistent with the photoemission spectrum.[1] According to the Dewar-Chatt-Duncanson scheme[7] for a π complex, electrons of this level are donated to the metal, forming a σ bond, and donated back from the metal into the empty π^* level of C_2H_4, giving rise to a π bond. Both these components of the Ni-ethylene bond may be identified from contour plots [Figs. 2(a) and 2(c)]. As found in Zeise's anion,[4] but to a much lesser degree, the π level also mixes into other orbitals, especially the a_1 level contributing most to the Ni-Ni bond [Fig. 2(b)]. The metal-ethylene bond in this π complex is therefore expected to be weaker than in Zeise's anion.

For the di-σ complex we find essentially the same two-way interaction mechanism, giving rise however to two σ bonds, one from each carbon atom to the corresponding Ni atom. The charge donation from the ethylene π level is equally as strong as in the π complex, but divided among the two Ni atoms [Figs. 3(a) and 3(b)]. On the other hand, the backdonation from a Ni_2 antibonding level to the π^* orbital of ethylene is approximately 50% greater than in the π complex, leading to a weaker C-C bond [Fig. 3(c)].[11]

The shift of the ethylene π level due to π-d bonding has been derived from the photoemission spectrum of chemisorbed ethylene to be $\Delta\epsilon_{\text{exp}} = 0.9 \pm 0.1$ eV.[1] In the $X\alpha$-SW approach, ionization potentials are normally calculated by invoking Slater's transition-state procedure,[3] and thereby taking relaxation effects into account. For comparable systems this relaxation is found to be nearly equal.[12] As the ethylene subunit is preserved to a large degree in both model complexes, we estimate the shift of the ionization potential of the π level upon chemisorption by taking the difference of the corresponding $X\alpha$-SW orbital energies. The accuracy of this procedure should be sufficient to allow comparison with the value derived from measurements with an energy resolution $\Delta\epsilon \sim 0.1$ eV.[1,15] We find from our calculations that $\Delta\epsilon_\pi = 0.72$ eV for the π complex and $\Delta\epsilon_\sigma = 0.30$ eV for the di-σ complex.

The results of our calculation for the shift of the π level and the change in work function favor, when compared with the experimental values, the

π complex. The di-σ complex may play the role of a reaction intermediate for various surface reactions[9,10] because of its weaker C-C bond. The photoemission spectra[1] alone do not allow a discrimination between the two geometries for the "surface complex," as π-d interaction is possible in both cases.

These conclusions, however, have to be drawn with due caution. First of all, one might consider a systematic influence of the SCF-SW method on the results. It is important that only information about one-electron orbitals has been used. These have been shown generally to be in excellent agreement with experiment for a large variety of systems.[16] Furthermore, the model complexes used here are admittedly rather simple ones; one should increase the number of metal atoms to ensure a realistic description of the model "surface." Also, the geometry of the adsorbate should be varied, as it is known for instance that the ethylene subunit in Zeise's anion is not planar.[17] (The effect on the ionization potentials is expected to be minor.) As a next step the model presented here should be tested for different adsorbate molecules, e.g., acetylene and ethane, and various other metal substrates. Such investigations are under way and will be reported elsewhere. The calculations presented here have shown how a local-bonding approach to chemisorption[6] implemented with the SCF-$X\alpha$-SW method can yield unique information on the bonding of hydrocarbons to a metallic diatom.

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