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Interaction of Saturated Hydrocarbons with Transition-Metal Films: Molecular Orbital Calculations

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Abstract: Tight-binding-type calculations have been performed to treat the chemisorption and the C–H bond activation of saturated hydrocarbons (CH_4 and C_2H_6) on transition-metal films. The films contain two to five layers of metal atoms, each with a valence s, p, d component of orbitals. A metal–hydrogen–carbon attractive interaction exists, as manifested by a partial population of the σ^*_{C-H} antibonding hydrocarbon molecular orbitals providing an acceptor function for the molecule. This effect is characterized by a small net electron transfer to hydrocarbon and a decrease in the C–H overlap population. The chemisorption energy of a given hydrocarbon, CH_4 or C_2H_6, decreases as the d occupation of the metal film increases in traversing a periodic row from left to right. This effect may be traced to the fact that the separation between σ^*_{C-H} energy levels of hydrocarbon and metal film Fermi energy increases with increasing d occupation.

The interaction of saturated hydrocarbons with transition-metal surfaces is an area of active experimental research. This interest stems from the well-known reactivity patterns of such molecules. There are hydrogenolysis reactions[1] leading to smaller hydrocarbon molecules and C–H bond-breaking reactions such as CH_4 decomposition[2] or cyclohexane dehydrogenation.[3] Experimental studies of saturated hydrocarbons interacting with ordered surfaces of Ru(001),[4] Ir(110),[5] and Pt(111)[6] have been reported. The basic finding is that molecular adsorption at low temperature followed by molecular desorption below room temperature prevails except on the Ir(110)-(1 × 2) reconstructed surface.[5,7] On this surface hydrocarbons including ethane, propane, isobutane, and neopentane underwent C–H bond-breaking reactions at low temperature, indicating a catalytic mode for the metal surface.

Muetterties[7] has been particularly active in modeling the interaction of C–H bonds with transition metals with the use of cluster compound analogies. One particularly interesting example[8] concerns the molecule $HFe_4(\eta^2\text{-}CH)(CO)_{12}$, in which the bond lengths indicate the presence of a C–H–Fe three-center interaction. In a computational study[9] of this possibility, metal–hydrogen–carbon interactions were shown to contribute to the bonding of hydrocarbons on clean metal surfaces. It was proposed that these interactions play a role in C–H bond-breaking processes.

The purpose of this work is to probe the interaction of CH_4 and C_2H_6 with transition-metal surfaces having two-dimensional periodicity. In a molecular orbital framework the bonding mechanism would commonly be thought to involve either depopulation of σ_{C-H} bonding molecular orbitals or population of σ^*_{C-H} antibonding molecular orbitals. This work will examine these two possibilities by use of an LCAO-MO tight-binding type of calculation. Chemisorptive bonding geometry of the hydrocarbon will be examined and a mode of C–H bond activation presented. We begin by considering the method of calculation.

The Model Calculations

Table I. Parameters of the Calculation

atom	Slater orbital	$-H_{ii}$, eV	exponent
metal	4s	3	2.75
	4p	2	2.75
	3d	8	5.983 (0.5264)[a] 2.613 (0.6372)
C	2s	21.40	1.625
	2p	11.40	1.625
H	1s	13.60	1.300

M–M distance = 2.5 Å

C–H distance = 1.1 Å

Wolfsberg–Helmholz K: 1.75, intramolecular; 2.0, adsorbate–metal; 3.0, metal–metal

[a] A linear combination of two Slater orbitals represents the d metallic orbitals. Coefficients are given in parentheses.

We used an extended Hückel[10] version of a tight-binding type of calculation for films with periodicity in two dimensions. The tight-binding method provides an excellent representation for the metal d orbitals, which are predominantly responsible for the interaction with hydrocarbon in this model. Most of the calculations were made for an adsorbate layer interacting with two metallic layers, although five-layer films were used in several cases as discussed in the Appendix. No significant differences were found. The repeating unit cell is a four-atom unit, which is square for (100) surfaces and trapezoidal (60°) for (111) surfaces. Each metal atom has valence s, p, d orbitals with typical parameters given in Table I. Overlap integrals appropriate to first-row transition-metal elements are computed between all neighboring intraplanar and interplanar unit cells up to three bond lengths. Appropriate Bloch sums are computed[11] to set up the secular equation

$$\det(H - ES) = 0 \tag{1}$$

The diagonal H matrix elements are computed by using the values in Table I in the appropriate sums. Nondiagonal terms are computed from the Wolfsberg–Helmholz formula

$$H_{ij} = \tfrac{1}{2}KS_{ij}(H_{ii} + H_{jj}) \tag{2}$$

where the overlap elements (S_{ij}) are computed from the appropriate Slater orbitals.

A constant number of electrons per unit cell as determined by the value of the Fermi energy was maintained before and after chemisorption. In addition, the metal parameters are chosen so that the σ_{C-H} levels of hydrocarbon are positioned at an energy separation from the Fermi energy (E_F) consistent with experiment.[12] The adsorbate molecules were positioned above the metal lattice with a primitive (2 × 2) lattice to maintain negligible adsorbate–adsorbate interactions. The adsorbate layer covers only one surface of the metal film in these calculations, leaving the

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(1) Sinfeld, J. H.; Carter, J. L.; Yates, D. J. C. *J. Catal.* **1972**, *24*, 283.

(2) Kuijpers, E. G. M.; Jansen, J. W.; vanDillen, A. J.; Geus, J. W. *J. Catal.* **1981**, *72*, 75. Frennet, A. *Catal. Rev.—Sci. Eng.* **1974**, *10*, 37.

(3) Demuth, J. E.; Ibach, H.; Lehwald, S. *Phys. Rev. Lett.* **1978**, *40*, 1044. Tsai, M.-C.; Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 2539.

(4) Madey, T. E.; Yates, J. T., Jr. *Surf. Sci.* **1978**, *76*, 397.

(5) Wittrig, T. S.; Szuromi, P. D.; Weinberg, W. H. *J. Chem. Phys.* **1982**, *76*, 3305; **1982**, *76*, 716.

(6) Salmeron, M.; Somorjai, G. A. *J. Phys. Chem.* **1981**, *85*, 3835.

(7) Muetterties, E. L. *Chem. Soc. Rev. (London)* **1982**, *11*, 283.

(8) Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 773. Beno, M. A., Williams, J. M.; Tachikawa, M.; Muetterties, E. L. *Ibid.* **1981**, *103*, 1503.

(9) Gavin, R. M., Jr.; Reutt, J.; Muetterties, E. L. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 3981.

(10) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

(11) Baetzold, R. *Solid State Commun.* **1982**, *44*, 781.

(12) Demuth, J. E. *Surf. Sci.* **1979**, *80*, 367.

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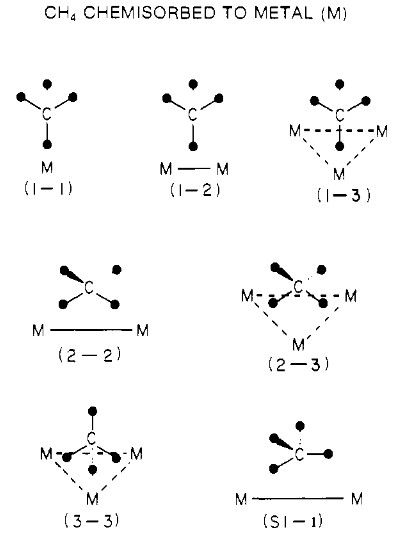

Figure 1. Geometric arrangements of CH_4 molecule relative to metal atoms (M).

second metal surface free. The effect of adding a second adsorbate layer is discussed in the Appendix.

The heat of adsorption is computed as the difference in separate and chemisorbed total energy (E)

$$E = \sum_i n_i \epsilon_i \qquad (3)$$

where n_i = occupation number and ϵ_i = eigenvalue. Dipole moments perpendicular to the surface of the metal are computed by the dominant one-center term

$$\langle p_z | z | d_{z^2} \rangle \qquad (4)$$

which involves p_z and d_{z^2} orbitals of the metal. The electron population of a given group of atoms is computed from the sum of squares of the occupied normalized eigenvectors appropriate to the atom(s) under consideration.

The computational procedure used here is similar to those reported earlier[13,14] for adsorbates on transition-metal films. In this semiinfinite method the number of cells in the surface (N) is finite and defines k values, $k = 2\pi m/Na$, with $-N/2 \leq m \leq N/2$, where a is the lattice constant. Thus for (100) surfaces we used the k values (0,0), $\pi/a(1,0)$, $\pi/a(0,1)$, and $\pi/a(1,1)$, and for (111) surfaces the k points (0,0), $\pi/a(1,-1/(3)^{1/2})$, $\pi/a(0,2/(3)^{1/2})$, and $\pi/a(1,1/(3)^{1/2})$ were used for the two-layer film calculations. A four-point grid was adopted for final calculations after calculation with more closely spaced k points gave essentially the same results. Calculations with five-layer films reported in the Appendix employed nine k points chosen similarly. The results are averaged after computation over k points.

Results

A. CH_4 Geometric Preference. Several of the high-symmetry bonding configurations for methane chemisorbed to the (111) and (100) surfaces of transition-metal films were surveyed. Figure 1 sketches these sites and defines a notation we will use throughout the paper. The (x–y) notation corresponds to x hydrogen atoms of methane interacting directly with a total of y metal atoms (M) on the surface where the gas-phase molecular geometry is retained. To further specify some of the cases, we state that the carbon atom lies along the perpendicular bisector of an M–M bond (1–2 and 2–2) or it is placed perpendicular to the center of a metal-atom triangle (1–3, 2–3, and 3–3). In the special case (S1–1) the C–H axis is parallel to a metal–metal bond with only one hydrogen atom interacting significantly with the metal surface. The metal–H bond lengths are taken as 1.7, 1.75, and 1.85 Å for single, double, and triple coordination, respectively, to metal atoms. These particular values are based upon data observed in organometallic compounds.[9,15] Nevertheless, our computed trends are not dependent upon accuracy of the particular M–H distance chosen. We find the same order of geometric preference upon proportionate increases in the bond length. Finally, although other geometric arrangements of chemisorbed molecules could have been tried, economy of effort restricted our attention to those in Figure 1.

Table II. Results for CH_4 Chemisorption on the Surface of Two-Layer Metal Films $s^{0.35}p^{0.37}d^{8.70}$ [a]

			pop.	
geometry	Q, eV	$\Delta\langle p_z \| z \| d_{z^2}\rangle$, au	CH_4 Δp, au	M[b] Δd, au
		111 Surface		
1-1	0.05	−0.045	+0.08	−0.15
1-2	−0.46	−0.025	+0.13	−0.12
1-3	−0.71	−0.008	+0.17	−0.07
2-2	−0.32	−0.041	+0.14	−0.13
2-3	−0.69	−0.030	+0.20	−0.12
3-3	−0.96	−0.045	+0.20	−0.18
		100 Surface		
1-1	−0.10	−0.043	+0.07	−0.11
1-2	−0.22	−0.009	+0.05	−0.09
1-4	−1.67	−0.24	+0.12	−0.12
2-2	−0.27	−0.007	+0.05	−0.06
3-4	−0.92	−0.017	+0.07	−0.09

[a] Parameters of Table I with $E_F - \epsilon_d$ = 2 eV. [b] M is a metal atom in direct contact with part of the CH_4 molecule.

The chemisorption energies in Table II show that methane chemisorbs preferentially on the (100) and (111) surfaces with a minimal number of M–H contacts. The (1–1) geometry is preferred for this metal with a nearly full d band. We attach greatest significance to the trends in values among different sites rather than the specific absolute values.

B. Dipole Moment. The dipole moment of a surface metal atom becomes more negative upon CH_4 chemisorption. The data in Table II show that the change in the dominant p_z, d_{z^2} matrix element is negative as a result of the CH_4 interaction. The methane molecular orbitals mix more of the metal p orbitals into the occupied states, causing rehybridization of the surface metal atom similar to that observed in earlier calculations for H atoms interacting with suface atoms.[16] Apparently atomic and molecular chemisorption are equally effective in changing the dipole moment. A decrease in dipole moment perpendicular to the surface can be associated with a decrease in work function. A rough estimate of the work function change is 1 eV/0.06 au change in dipole moment.[17] A decrease in work function of −0.5 eV has been reported for cyclopropane adsorbed on the Ir(110) surface.[5] This direction is consistent with our calculations and follows the lines of a perturbation analysis[18] presented earlier.

C. Electron Population. An increase in the electron population of CH_4 is observed at the expense of the d-electron population of metal atoms with which there is direct CH_4 interaction as shown in Table II. This effect occurs with each geometry on both (100) and (111) surfaces. It is the result of mixing antibonding σ^*_{C-H} molecular orbitals with the occupied metal d orbitals in dominance to the mixing of σ_{CH} molecular orbitals with unoccupied metal levels. Accompanying the decrease in d population of the metal atom(s) directly interacting with the hydrocarbon is a smaller increase in sp population. The d population of atoms in the second layer, not in direct contact with the hydrocarbon, has only minor sensitivity to the presence of adsorbate. Thicker films, treated in the Appendix, show that film thickness is not a major deter-

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(13) Fassaert, D. J. M.; van der Avoird, A. *Surf. Sci.* **1976**, *55*, 291.

(14) Kobayashi, H.; Yoshida, S.; Kato, H.; Fukui, K.; Tarama, K. *Surf. Sci.* **1979**, *79*, 189.

(15) Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. *Acc. Chem. Res.* **1979**, *12*, 176.

(16) Baetzold, R. C. *J. Phys. Chem.*, accepted for publication.

(17) $\Delta\phi \simeq e\Delta\langle p_z|z|d_{z^2}\rangle$; see ref 16 for details.

(18) Shustorovich, E. *J. Phys. Chem.* **1982**, *86*, 3114. Shustorovich, E.; Baetzold, R. C. *Appl. Surf. Sci.* **1982**, *11/12*, 693.

Table III. Parameters Chosen To Simulate N_d Changes in the Metal Film[a]

$-H_{dd} = -\epsilon_d$, eV	$-E_F$, eV	N_d
5.0	5.0	4.80
6.5	5.5	7.84
8.0	6.0	8.70
9.5	6.5	9.58

[a] $\epsilon_s = -3$ eV, $\epsilon_p = -2$ eV.

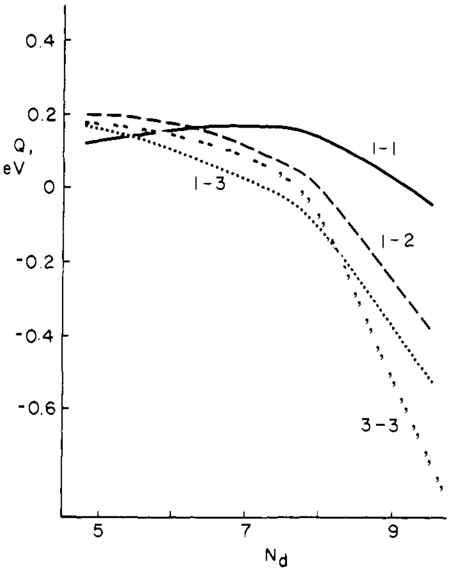

Figure 2. Heat of CH_4 chemisorption on a (111) face-centered cubic two-layer film as a function of the number of d valence metallic electrons (N_d) for several bonding geometries.

minant of properties of the chemisorbed state.

We wish to determine the behavior of chemisorbed hydrocarbon on transition-metal surfaces as one proceeds across a given period of a transition series. Thus, we must develop a procedure that allows us to simulate films containing atoms with different numbers of d electrons. Using earlier calculations,[11] derived from analysis of experimental work function and band structure data,[19] we simulate increasing N_d by decreasing the atomic d level (ϵ_d) simultaneously with smaller decreases in the Fermi energy (E_F). The relevant parameters for bare films are shown in Table III.

Variation of the metal d occupation results in different geometric preferences and heats of chemisorption. Figure 2 compares the heat of chemisorption for four different sites as a function of N_d. We observe a preference for the (2–1) geometry compared to (1–1) at sufficiently small values of d occupation of the metal. There is a considerable increase in stability of the multicenter bonding configurations with decreasing values of N_d. In addition, the heat of chemisorption increases as N_d decreases. This behavior is consistent with the dominant acceptor mechanism leading to electron population of σ^*_{C-H}. This behavior was reported earlier[11] for atomic adsorbates and is due to the fact that the energy separation between σ^*_{C-H} and E_F increases as N_d increases. Thus the partial electron transfer to σ^*_{C-H} becomes smaller as N_d increases.

The computed net charge on the CH_4 molecule is negative for the values of N_d studied in Figure 3. The change in slope of the CH_4 charge is a reflection of two competing mechanisms: the number of d electrons of the metal available for transfer to CH_4 and the energy separation between E_F and σ^*_{C-H}, described above. The first mechanism becomes more likely with increasing N_d, but the second mechanism becomes less likely, as described above. Comparison of Figures 2 and 3 also shows that the heat of chemisorption and net charge transfer do not have a simple relationship, which reflects the fact that the heat of adsorption represents the sum of donor and acceptor contributions, whereas net charge transfer represents the difference.

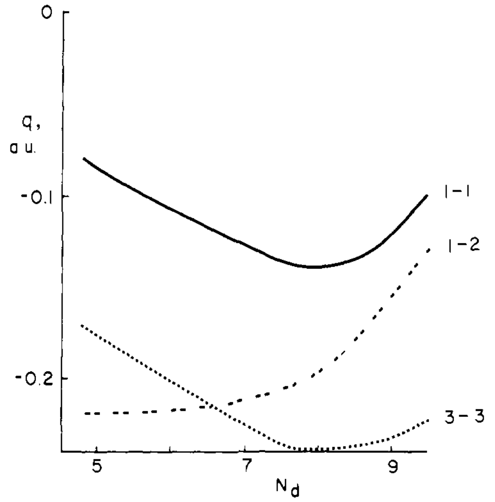

Figure 3. Net charge on CH_4 chemisorbed on a (111) face-centered cubic two-layer film as a function of N_d.

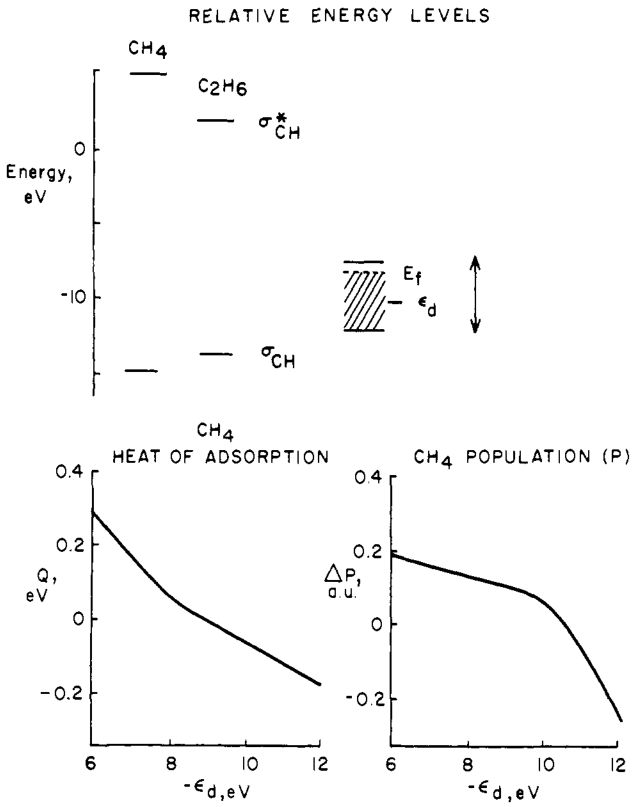

Figure 4. Computed energy positions for σ and σ^* levels of CH_4 and C_2H_6. The metallic d band is arbitrarily shifted up or down in energy by changing ϵ_d while keeping $E_F - \epsilon_d = 2$ eV constant. The heat of chemisorption and change in CH_4 electron population are shown as a function of $-\epsilon_d$.

The acceptor mechanism through σ^*_{CH} was tested by performing hypothetical variations in the position of the metal d band. In Figure 4 the position of the d band is shifted while $E_F - \epsilon_d$ is kept constant. As the separation between the σ^*_{C-H} level and E_F decreases, more electrons are transferred to CH_4 and the heat of chemisorption increases. This behavior is expected for a predominant acceptor mechanism, since the acceptor ability of the molecule would be expected to decrease as $\sigma^*_{C-H} - E_F$ decreases.

D. Metal–H Interaction. The overlap population provides a measure of the interaction of hydrogen atoms in CH_4 with the metal surface. We observe a positive value of 0.03–0.04 of the M–H overlap population for all N_d values, indicative of an M·

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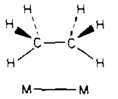
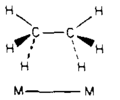
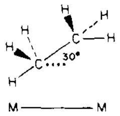
(19) Varma, C. M.; Wilson, A. J. *Phys. Rev. B: Condens. Matter* **1980**, *22*, 3795.

Table IV. Effect of Bending Noninteracting Hydrogen Atoms toward the Surface for Chemisorbed CH_4 (1-1) Geometry

site	N_d	bending angle	Q, eV
1-1	8.7	0	0.05
1-1	8.7	5	−0.46
1-2	8.7	0	−0.46
1-2	8.7	5	−0.90
1-3	8.7	0	−0.71
1-3	8.7	5	−1.11
1-1	4.8	0	+0.27
1-1	4.8	5	−0.39
1-2	4.8	0	+0.13
1-2	4.8	5	−0.22
1-3	4.8	0	+0.43
1-3	4.8	5	+0.04

Table V. Properties of Ethane Chemisorbed to Two-Layer (111) Surface

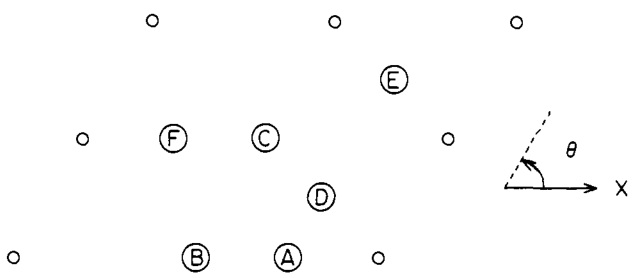
structure	geometry	N_d	Q, eV	change in C_2H_6 pop. Δp, au
	1	4.80 7.84 8.70 9.58	0.18 0.17 0.03 −0.11	+0.13 +0.21 +0.20 +0.16
	2	8.70	−0.94	+0.34
	3	8.70	−0.01	+0.10

··H–C interaction in accord with the earlier work of Muetterties.[7–9] Along with the presence of a positive M···H–C overlap population we find a decrease in the C–H overlap population for H atoms interacting with metal atoms. The typical change is from 1.24 to 1.19 for the sites in Table II on the (111) surface. This result is in accord with the population of σ^*_{C-H} molecular orbitals and weakening of the C–H bond. Such an effect should be observed in the vibrational frequencies of the chemisorbed molecule.

E. Deformation of CH_4 Structure. The presence of an M···H interaction does not distort the tetrahedral CH_4 structure. Table IV shows data for the (1–1) site where the three H atoms pointing away from the surface are bent towards the surface by 5° from the tetrahedral structure. In each case the molecule is destabilized by this small deformation. We have examined several other deformation modes, and in each case the molecule is destabilized. Thus, we must conclude that the M···H interaction is not strong enough to significantly deform the rigid CH_4 geometry.

F. C_2H_6 Adsorption. We begin the study of ethane interactions with transition-metal films by considering various geometries of the molecule on a cluster. A 12-atom metal cluster, sketched in part in Figure 5, contains nine atoms in the surface plane and three atoms beneath. We consider various sites for adsorption in Figure 5, where the ethane molecule is taken in an eclipsed geometry with a single H atom on each C atom interacting with the surface. Two sets of metal parameters were used to determine adsorption energy. Although there are some differences among the various adsorption sites, the adsorption energies do not differ greatly. Also, as the metal atomic orbital energies become more negative, the molecule is bound less strongly. Finally, we have chosen site A for investigation on film surfaces because it is one of the more energetically favored sites that can be treated well in our model.

The adsorption energy of ethane on (111) films is shown in Table V. A minimal (1 H/C vs. 2 H/C) contact of hydrogens with the surface is preferred for the ending transition-metal elements (N_d = 8.70). There does appear to be a benefit (0.04 eV) from a ring-type structure (MHCCHM), as may be seen by comparing the Q values for the tipped ethane (geometry 3) with those of the parallel molecule (geometry 1). In addition, the heat of chemisorption is largest on the films with the smallest N_d values. This phenomenon is consistent with the net electron transfer from metal to ethane orbitals. As the E_F value becomes less negative (smaller N_d), the energy gap between E_F and σ^*_{C-H} of the ethane molecule becomes smaller, leading to greater interactions and apparently larger Q values. This effect was noted in earlier calculations for atomic adsorbates.[11]



Site	Angle with Respect to X-axis	Q(eV) Parameter 1	Q(eV) Parameter 2
A	0	−0.19	0.46
B	0	−0.38	0.48
C	−30	−0.44	0.46
C	−60	−0.63	0.24
D	−60	−0.20	0.44
E	−30	−0.85	0.11
F	−90	−0.25	0.87

Figure 5. Top layer of a 14-atom cluster model is shown as well as various sites for the chemisorbed C_2H_6 molecule. The closest M–H distance is 1.8 Å, and the M–M distance is 2.5 Å. The heats of chemisorption (Q) are shown for the d^9 metal atom with two sets of parameters. The site designation refers to the projection of the midpoint of the C–C bond parallel to the surface, and θ is the angle with respect to the x axis defined in the inset. Note that metal atoms are present (but blocked from view) under sites B and C. The coulomb integrals are as follows: parameter set 1, $-H_{ss}$ = 5 eV, $-H_{pp}$ = 4 eV, $-H_{dd}$ = 10 eV; parameter set 2, $-H_{ss}$ = 3 eV, $-H_{pp}$ = 2 eV, $-H_{dd}$ = 8 eV.

G. C_2H_6 Dissociation. The population of σ^*_{C-H} orbitals of ethane provides a mechanism for C–H bond activation. Population of antibonding molecular orbitals weakens the C–H bond. We have attempted to simulate this process by computing a hypothetical reaction coordinate for H dissociating from C_2H_6. We consider a least-motion pathway for moving one of the H atoms interacting with a metal atom (geometry 1, Table V) to a site in a threefold hollow between three metal atoms. The energy computed for this pathway is shown in Figure 6. Of course, since our method of calculation is approximate and the reaction coordinate is hypothetical, we must be careful not to deduce too much from this profile. The small activation barrier seems to be significant, and the transition state lies close to the reactants. The electron donation to σ^*_{C-H} levels of C_2H_6 is consistent with this mechanism, since it provides a driving force for dissociation and should stabilize the intermediate state where the incipient H· and C_2H_5· radical species are forming. Both of these species accept electron density from the metal. The effect of N_d on the dissociation reaction is particularly significant, since the most stable radical species are formed on surfaces of smallest N_d. We expect these surfaces to show the greatest ability to dissociate C_2H_6.

Discussion

These calculations have suggested that saturated hydrocarbons act predominantly as acceptors of electron density from transition-metal surfaces. Although this role has not been previously assigned to saturated hydrocarbons, an acceptor mechanism is generally accepted[20] for molecules such as CO on transition-metal

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(20) Blyholder, G. J. Phys. Chem. **1964**, 68, 2772.

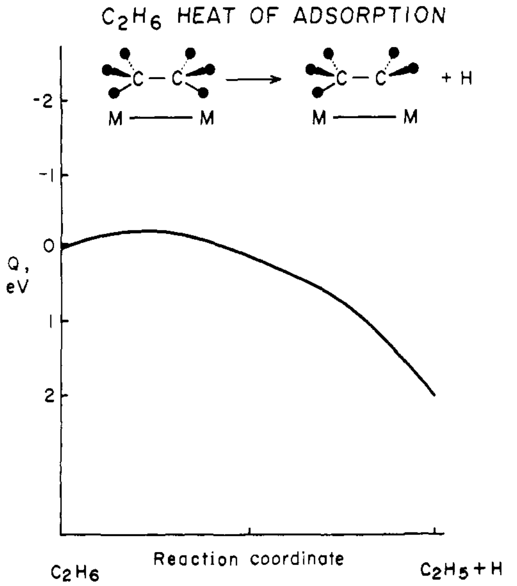

Figure 6. Reaction coordinate for C_2H_6 dissociation to C_2H_5 and H on the (111) surface; $N_d = 8.70$. The starting geometry of C_2H_6 is defined by geometry 1 in Table V. The Cartesian coordinates (Å) of the dissociating H are as follows: initial $x_0 = -0.123$, $y_0 = 0.00$, $z_0 = 1.696$; final $x = 0.625$, $y = 1.443$, $z = 1.407$ relative to the closest metal atom at the origin. The percentage change in $x - x_0$, $y - y_0$, and $z - z_0$ is kept equal for each point on the reaction path and plotted as the abscissa.

surfaces. In saying that the σ^*_{C-H} levels of the saturated hydrocarbon act as an acceptor of electron density, we must remember that the σ_{C-H} levels are simultaneously acting as a donor. This effect may be uncovered from Figure 4. When the d levels of the metal are shifted sufficiently negative to bring them close in energy to the σ_{C-H} levels, the hydrocarbon becomes electron deficient. This corresponds to predominant donation from the σ_{C-H} levels of CH_4. This situation does not represent most transition-metal surfaces, because the metal energy levels have significant separation from the σ_{C-H} levels. The energy separation $E_F - \sigma_{C-H} = 8$ eV measured[12] by UPS on Pt(111) is estimated to hold on the 3d transition metals for which our calculations are most appropriate. For other energy separations, the direction of net charge transfer could be derived from the $E_F - \sigma_{C-H}$ values by using Figure 4. A better analogy for dominant σ_{C-H} bonding occurs for the metal d energy levels in high-oxidation-state organometallic clusters.[21] Here the metal energy levels are close to the ligand σ_{C-H} levels, and positive charge on the hydrocarbon is possible.

There is little experimental evidence with which to test the prediction of an acceptor mechanism for saturated hydrocarbons on transition-metal films. The magnitudes computed for the heats of adsorption are realistic compared to experimental values. Ethane chemisorbed to Ru(001) has a heat of adsorption of 5 kcal/mol,[4] which agrees well with the value 0.17 eV $\simeq$ 4 kcal in Table V for a surface of approximately d^8 occupation number. In addition, the model property predicts the sign of work-function change without using any arguments based upon charge transfer. Lack of experimental structural assignments prevents testing this part of the calculation. We do not regard this as critical, since the behavior of hydrocarbon did not change significantly with site on the surface.

These calculations have supported the idea of Muetterties[7-9] that M···H–C interactions exist between saturated hydrocarbons and transition-metal surfaces. The interaction is weak for molecular species, but as the hydrocarbon dissociates, it may play a significant role in stabilizing intermediate species. In H dissociation from the (S1-1) structure of CH_4, a ring species $(\overline{M\cdots H\text{–}C\cdots M})$ is formed in which there is a positive overlap population among all of the directly interacting atoms. This effect operates in C_2H_6 dissociation and may be typical of transition states for dissociation.

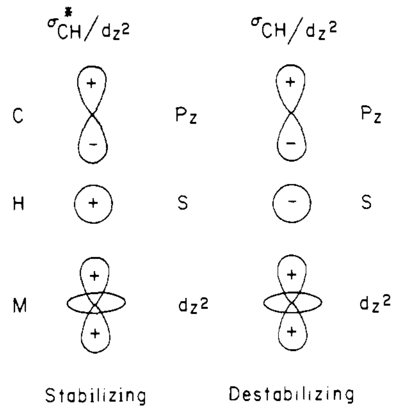

Figure 7. Interaction of a σ^*_{C-H} level or a σ_{C-H} level with a metal d_{z^2} orbital is stabilizing or destabilizing, respectively.

In a recent analysis of linear diatomic bonding for an on-top site, Shustorovich[22] has shown that the σ^* levels of a diatomic molecule such as N_2 produce a greater binding energy contribution than the σ levels. Using similar arguments within a perturbation analysis, we may show from a simple argument how electron transfer occurs predominantly to CH_4. Consider the (1-1) geometry of CH_4 bonded to one metal atom, where only the d_{z^2} interactions with σ_{CH} or σ^*_{C-H} molecular orbitals need to be considered. We note that bonding (σ^*_{C-H}/d_{z^2}) and antibonding (σ_{C-H}/d_{z^2}) interactions depicted in Figure 7 compete to donate electrons to or withdraw electrons from the C–H bond, respectively. From perturbation theory,[23] the d_{z^2} orbital will be mixed with wave functions

$$d_{z^2} + \lambda^* \sigma^*_{C-H} - \lambda \sigma_{C-H} \tag{5}$$

$$\lambda^* = \frac{\langle \sigma_{C-H}|H|d_{z^2}\rangle}{\epsilon_{\sigma^*_{C-H}} - \epsilon_d} \tag{6}$$

$$\lambda = \frac{\langle \sigma_{C-H}|H|d_{z^2}\rangle}{\epsilon_d - \epsilon_{\sigma_{C-H}}} \tag{7}$$

Thus the ratio λ^*/λ determines whether C–H is an acceptor (>1) or a donor (<1)

$$\frac{\lambda^*}{\lambda} = \frac{\langle \sigma^*_{C-H}|H|d_{z^2}\rangle}{\langle \sigma_{C-H}|H|d_{z^2}\rangle} \, \frac{\epsilon_d - \epsilon_{\sigma_{C-H}}}{\epsilon_{\sigma^*_{C-H}} - \epsilon_d} \tag{8}$$

The first ratio in eq 8 is given approximately by the ratio of the coefficients of the 1s orbital of H in the σ^* and σ levels of CH_4. This has the value 2, as derived from extended Hückel calculations. Note that this value is much greater than one because of the different normalization constants in the σ^* and σ molecular orbitals. Thus the σ level computed at −15.4 eV and the σ^* level computed at 3.6 eV define a point −9.1 eV, above which ϵ_d values produce an acceptor molecule and below which ϵ_d values give a donor molecule. This simple example shows that for most transition metals CH_4 will be an acceptor because $\epsilon_d > -9.1$ eV. Of course, this is a highly simplified model of the metal film designed only to show the physics of the interaction.

To test these ideas further, we examined NH_3, a molecule commonly thought to be an electron donor on transition-metal surfaces.[24] Several experimental studies have placed the molecule in a C_{3v} site with H atoms staggered with respect to metal on the (111) surfaces of Ni[25] and Ir.[26] It is thought that the N end of

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(21) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stilk, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857, and references therein.

(22) Shustorovich, E. *J. Phys. Chem.* **1983**, *87*, 14.

(23) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

(24) Fisher, G. B. *Chem. Phys. Lett.* **1981**, *79*, 452.

(25) Seabury, C. W.; Rhodin, T. N.; Purtell, R. J.; Merrill, R. P. *Surf. Sci.* **1980**, *93*, 117.

(26) Purtell, R. J.; Merrill, R. P.; Seabury, C. W.; Rhodin, T. N. *Phys. Rev. Lett.* **1980**, *44*, 1279.

Table VI. Results for CH_4 Chemisorption on the (111) Surface of Five-Layer Metal Films $s^{0.15}p^{0.09}d^{8.64}$

				pop.	
geometry	no. of adsorbate layers	Q, eV	$\Delta\langle p_z \mid z \mid d_{z^2}\rangle$, au	CH_4 Δp, au	M^a Δd, au
1-1	1	0.01	−0.011	+0.03	−0.04
1-1	2	0.02		+0.03	−0.04
1-2	1	0.20	−0.033	+0.09	−0.13
1-3	1	0.24	−0.028	+0.10	−0.13
1-3	2	0.24		+0.10	−0.12
2-2	1	−0.03	−0.030	+0.05	−0.09
2-3	1	0.09	−0.034	+0.05	−0.09
3-3	1	0.07	−0.031	+0.07	−0.13

[a] M is a metal atom in direct contact with part of the CH_4 molecule.

Table VII. Populations (au) of Metal Atoms in Five-Layer Films for CH_4 Adsorption on the 1–3 Site

layer no.	bare (111) film		(111) film plus one CH_4 layer		(111) film plus two CH_4 layers	
	sp	d	sp	d	sp	d
1	0.24	8.64	0.27	8.51	0.27	8.52
2	0.36	8.22	0.36	8.22	0.37	8.22
3	0.40	8.19	0.39	8.19	0.39	8.19
4	0.36	8.22	0.36	8.22	0.37	8.22
5	0.24	8.64	0.24	8.64	0.27	8.52
1	0.37	5.00	0.42	4.77	0.39	4.81
2	0.63	5.31	0.63	5.38	0.63	5.34
3	0.75	5.61	0.78	5.62	0.78	5.60
4	0.63	5.31	0.63	5.28	0.63	5.34
5	0.37	5.00	0.37	4.98	0.39	4.81

the molecule is toward the surface. We have found a significant acceptor role for NH_3 in preliminary calculations on the film surfaces. Potential-energy calculations are not yet complete, so let us only consider the molecule in its gas-phase geometry above a C_{3v} site on a (111) surface having the N–M distance of 2.0 Å. Under this circumstance we compute a binding energy of 0.26 eV and an increase in electron population of the ammonia of +0.3. On the typically $d^{7.9}$ metal a small decrease in d population takes place. These results are only preliminary, since a significant metal–hydrogen interaction is found, which could distort the NH_3 molecule. Note that this value is much greater than one because of the different normalization constants in the σ^* and σ molecular orbitals. Nevertheless, these results show that a significant acceptor role may exist for several molecules chemisorbed on transition-metal films even though they are commonly thought of as donors.

This first calculation of the interaction of saturated hydrocarbons with transition-metal surfaces has uncovered the importance of the role of the adsorbate antibonding molecular orbitals. The method used is crude, but the results are chemically significant and can serve as a basis for further experimental or theoretical study. These results are also found in independent model studies,[22] and their applications will be discussed in a separate paper.[27] The interpretation of values rests upon computed *trends* rather than absolute values.

Acknowledgment. I am grateful to Earl Muetterties and Evgeny Shustorovich for many valuable discussions concerning this work. Roald Hoffmann has generously given advice and comments contributing to this work.

Appendix

Calculations for five-layer metal films were undertaken to determine whether there is a dependence of the computed trends on film thickness. The thicker films have a unit cell with one atom per layer. No direct adsorbate–adsorbate interactions were computed, in order to better simulate the low adsorbate coverage on the two-layer films. Calculations were performed where just one or both of the metal surfaces were covered by an adsorbate layer. The results of this type of calculation for methane adsorption are shown in Table VI. A close correspondence with the results on two-layer films is noted. Methane accepts electrons from the d orbitals of metal atoms with which it has direct interaction, and the chemisorption-induced dipole is negative. The stereochemistry of adsorbed methane maintains minimal hydrogen contact. The delicate nature of the adsorbate registry is revealed by the preferred 1–3 site on the thicker film. Finally, the presence of an adsorbate layer adsorbed to both sides of the metal film does not significantly alter the computed properties.

More extensive calculations of the electron population have been carried out to further test the approximation of using one adsorbate layer. Table VII reports electron populations for five-layer films of middle and ending transition elements before and after chemisorption of CH_4 on the 1–3 site. The population is very stable for the nearly full d occupation metal, but this is less so on the half-full d element. Nevertheless, the use of one adsorbate layer seems satisfactory for a weakly electron-withdrawing adsorbate such as CH_4.

Registry No. CH_4, 74-82-8; C_2H_6, 74-84-0.

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(27) Shustorovich, E.; Baetzold, R. C.; Muetterties, E. L., *J. Phys. Chem.* **1983**, *87*, 1100.