Performance of the B3LYP/ECP DFT Calculations of Iron-Containing Compounds

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Iron-containing molecules and ions with various types of bonding were calculated using DFT theory (B3LYP functional) and an energy-adjusted effective core potential for iron (ECP(S)). Examination of calculated geometries, bond dissociation energies, ionization energies, enthalpies of formation, and harmonic frequencies and their comparison with experimental and higher level (CCSD(T), MCPF, CASSCF) computational data show that B3LYP/ECP(S) calculations of iron-containing species are capable of giving reliable results. The dissociation energies were calculated for iron-containing species with various bonding interactions having experimental estimates of bond strengths varying from 5.0 (Fe^+-H_2) to 99.5 kcal/mol (Fe^+-CH), i.e., within a range of 95 kcal/mol, do not reveal any systematic trends in the errors. The average absolute deviation is 4.6 kcal/mol. The maximum deviation from the experimental D_0 value is +8.0 kcal/mol for Fe^+-CH. This experimental estimate, however, has an uncertainty of ±7 kcal/mol. The B3LYP/ECP(S) calculated enthalpies of formation have an average absolute deviation of 5.7 kcal/mol with the largest deviation of 14 ± 7 kcal/mol of the experimental $\Delta H_{f\,0}$ value in the case of $FeCH^+$. Geometries and harmonic frequencies calculated using the B3LYP/ECP(S) scheme are generally in good agreement with the available experimental data or with results of higher level calculations.

1. Introduction

Accurate calculations of transition metal complexes have been a challenging problem in theoretical chemistry.[1] Recent years have witnessed encouraging results of applications of density functional theory (DFT)[2] methods to metal complexes, employing both "gradient-corrected"[3] and hybrid approaches[4] in which the Hartree−Fock "exact exchange" is also included in the functional.[5−8] Among various proposed functionals, the Becke's three-parameter hybrid functional[3a,4a] combined with the Lee, Yang, and Parr (LYP) correlation functional,[3b] denoted as B3LYP,[4b] appears to be the form which yields good results in calculations of atomization energies,[9] proton affinities,[10] harmonic frequencies of polyatomic molecules,[11] and binding energies of species containing first-row transition metals.[6a,e,7b] The binding energies for iron-containing species calculated using the B3LYP functional were found[6b] to be in a better agreement with experimental data than the results obtained at the MP2 level. Transition metal species may exhibit multireference character and require treatments that take into account nondynamical correlation. Density functional methods based on nonlocal functionals appear to be capable of providing a reliable description of such systems.[1b,9h−l]

Effective core potentials (ECP)[12] provide a way to reduce difficulties in calculations of species containing heavy atoms, which are caused by a large number of two-electron integrals.[1,13] It is also important that relativistic or quasi-relativistic ECPs can reflect (to some extent) relativistic effects upon geometries and bond energies.[12−14] Quasi-relativistic ECP parameters are derived, as a rule, from quasi-relativistic calculations for atoms and monatomic ions, in which the mass−velocity term and Darwin terms are taken into account as the most important relativistic terms of the Dirac−Fock Hamiltonian.[15] ECP calculations can achieve nearly the same or sometimes even better accuracy than all-electron calculations with large basis sets when the same level of theory is used to describe correlation effects.[16−18]

Here we report results of an approach which combines advantages of using both DFT and ECP in calculations of transition-metal species (denoted as B3LYP/ECP). As calculations of species containing first-row transition metals often encounter much greater difficulties to reach an acceptable accuracy than in the case of calculations on compounds formed by the second- and third-row transition metals,[1b,8a,19] we have chosen iron-containing species with various ligands, which exemplify a wide variety of bonding patterns. An additional reason to choose these species was that a larger number of experimental data are available for them compared with complexes formed by other first-row transition metals. While the MRCI/CASSCF, ACPF/CASSCF, MCPF, QCISD(T), and CCSD(T) methods give generally accurate data for transitional metal species containing two or three heavy atoms,[1b,6b,20] their requirements for computer time often make these methods prohibitively expensive for calculations on larger systems of experimental and industrial interest. In the present study we examine the performance of the B3LYP/ECP scheme in order to find out whether this approach can be a promising alternative to methods more demanding of computer resources.

2. Computational Methods

Ab initio molecular orbital calculations[21] were performed with the GAUSSIAN 94 system of programs.[22] The Becke's three-

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parameter hybrid functional[4a] combined with the Lee, Yang, and Parr (LYP) correlation functional,[3b] denoted B3LYP,[4b] was employed in the calculations using density functional theory (DFT):

$$E_{xc}^{B3LYP} = (1 - a_0)E_x^{LSDA} + a_0E_x^{HF} + a_x\Delta E^{B88} + a_cE_c^{LYP} + (1 - a_c)E_c^{VWN} \quad (1)$$

$$(a_0 = 0.20; \quad a_x = 0.72; \quad a_c = 0.81)$$

In eq 1 E_x^{HF} is the Hartree−Fock exchange, E_x^{LSDA} denotes the local (Slater) exchange energy from local spin density approximation (LSDA), ΔE^{B88} is Becke's gradient correction to the exchange functional,[3a] E_c^{LYP} is the correlation functional developed by Lee, Yang, and Parr,[3b] and E_c^{VWN} is the correlation energy calculated using local correlation functional of Vosko, Wilk, and Nissair (VWN).

For iron the energy-adjusted quasi-relativistic effective core potential (ECP) developed by the Stuttgart group[23] was used (denoted further as ECP(S)). This ECP simulating the influence of the Ne-like core, Fe^{16+}, on the $3s^23p^63d^64s^2$ ($3d^74s^1$) valence shell was derived using atomic excitation and ionization energies.[23a] Applicability of the ECPs generated from Hartree−Fock atomic calculations to DFT calculations has been shown recently.[24] Geometries were optimized[25] at the B3LYP level using the 6-311G(d,p) basis set (the 6-311G(d,2p) basis set was used for FeH_n species)[21] and the (8s7p6d)/[6s5p3d] valence basis set[23a] for the first- and second-row main-group atoms and for iron, respectively. The 6-311+G(3df,2p) basis set for main-group atoms and the (8s7p6d2f)/[6s5p4d2f] valence basis set for iron[23b] were used to calculate final energies. In some cases for the sake of comparison we carried out calculations using BD(T) (Brueckner doubles including a perturbation correction for triple excitations),[26] QCISD(T),[27] and CCSD(T)[28] levels of theory. The stationary points on the potential energy surfaces were characterized by calculations of vibrational frequencies, which were done numerically in the ECP calculations of iron-containing species at the B3LYP level. Enthalpy−temperature corrections were derived using harmonic frequencies which were computed at the B3LYP/6-311G(d,p) level and scaled by 0.98 according to Bauschlicher and Partridge[9b] and standard statistical thermodynamics formulas.[21,29] Theoretical enthalpies of formation at 0 and 298 K, $\Delta H_{f\,0}$ and $\Delta H_{f\,298}$, respectively, were derived from calculated B3LYP atomization energies for the species at 0 or 298 K and standard experimental enthalpies of formation for the atoms at 0 or 298 K, respectively. Experimental temperature corrections for atoms, taken from ref 30, were used. The compendium of Lias et al.[31] was used as the source of thermodynamical data unless stated otherwise. Throughout the text, bond lengths are in angstroms and bond angles are in degrees.

It would be reasonable to examine the performance of the B3LYP calculations for some main-group compounds for which experimental data have been well-established, before considering iron-containing compounds for which the experimental data are relatively scarce and are not always accurate. The enthalpies of formation for methine, methylene, methyl, methane, carbon monoxide, ethane, ethylene, and acetylene as well as the bond dissociation energies for ethane, ethylene, and acetylene calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-311G(d,p) + ZPE(B3LYP/6-311G(d,p)) level are given in Tables 1 and 2. Methine, methylene, carbon monoxide, and ethane are the ligands in iron complexes considered below. As seen from these tables, the calculated enthalpies of formation agree well with the experimental values. The average absolute deviations for the $\Delta H_{f\,0}$ and $\Delta H_{f\,298}$ values are 1.45 and 1.48 kcal/mol, respectively. The largest deviation is −3.3 kcal/mol in the case of CO. The calculated bond energies show reasonably good agreement with the experimental values. The largest deviation is the underestimation of the C−C bond energy in ethane by 5.3 kcal/mol. The C≡C bond energy in acetylene is underestimated by 5.1 kcal/mol (Table 2). For the C═C bond dissociation energy in ethylene the B3LYP/6-311+G(3df,2p) calculations lead to results comparable in accuracy with G2 calculations.[32] Therefore, we can conclude that the B3LYP calculations are capable of providing reliable estimates of formation enthalpies and bond dissociation energies for the simplest hydrocarbons.

TABLE 1: B3LYP Calculated and Experimental Enthalpies of Formation (in kcal/mol) of Methine, Methylene, Methyl Radical, Methane, Carbon Monoxide, Ethane, Ethylene, and Acetylene[a,b]

molecule	$\Delta H_{f\,0}$ (calc)	$\Delta H_{f\,0}$ (exptl)	Δ_1[c]	$\Delta H_{f\,298}$ (calc)	$\Delta H_{f\,298}$ (exptl)	Δ_2[d]
CH	140.10	141.6	1.50	140.91	142.4	1.41
$CH_2(^3B_1)$	91.69	93.0	1.31	91.79	93.0	1.13
CH_3	33.20	35.6	2.40	32.43	34.8 ± 0.3	2.29
CH_4	−16.94	−16.0	0.94	−18.86	−17.8 ± 0.1	0.97
CO	−24.12	−27.20	−3.08	−23.32	−26.42	−3.31
ethane	−15.87	−16.4	−0.53	−19.67	−20.1 ± 0.05	−0.59
ethylene	14.53	14.5	−0.03	12.47	12.5 ± 0.2	−0.13
acetylene	56.53	54.7	−1.83	56.36	54.5 ± 0.25	−2.02

[a] ΔH_f values were calculated at the B3LYP/6−311+G(3df,2p)//B3LYP/6−311G(d,p) + ZPE(B3LYP/6−311G(d,p)) level. [b] Experimental values are taken from ref 31. [c] $\Delta_1 = \Delta H_{f\,0}(\text{exptl}) - \Delta H_{f\,0}(\text{calc})$. [d] $\Delta_2 = \Delta H_{f\,298}(\text{exptl}) - \Delta H_{f\,298}(\text{calc})$.

TABLE 2: B3LYP and G2 Calculated and Experimental Bond Dissociation Eneries (D_0, in kcal/mol) for the Carbon−Carbon Bonds in Ethane, Ethylene, and Acetylene

bond	B3LYP[a]	G2[b]	exptl
$H_3C{-}CH_3$	82.27	88.31	87.6[c]
$H_2C{=}CH_2$	168.8	174.4	171.01 ± 1.20[d] 171.9[c]
$HC{\equiv}CH$	223.66	226.27	228.80 ± 0.69[d] 229.8[c]

[a] Calculated at the B3LYP/6−311+G(3df,2p)//B3LYP/6−311G(d,p) + ZPE(B3LYP/6−311G(d,p)) level. [b] G2 values are taken from ref 32. [c] Experimental values are taken from ref 31. [d] For recent experimental estimates of the C═C and C≡C bond dissociation energies of ethylene and acetylene, respectively; see ref 33.

3. Results and Discussion

Atomic Excitation and Ionization Energies of Fe and Fe⁺. A fundamental requirement which a computational scheme must possess when applied to calculations of transition-metal species is its ability to correctly reproduce atomic excitation and ionization energies.[16,34] As seen from the data listed in Table 3, the $^5D-^5F$ excitation energy calculated at the B3LYP level using either the ECP(S)/[6s5p4d2f] valence basis set or all-electron (AE) basis set is underestimated whereas the QCISD(T) and CCSD(T) calculations resulted in overestimated values. Calculations using the MCPF approach give an exaltation energy of 27.0 kcal/mol.[6b] DFT and, particularly, B3LYP calculations are biased[6b,8,19] in favor of the $3d^7s^1$ configuration over the $3d^64s^2$ configuration of Fe. As a consequence, the calculated $^5D-^5F$ excitation energy is underestimated (Table 3). If the relativistic correction is added, which increases the calculated $Fe((^5D)-(^5F))$ excitation energy by 5.1 kcal/mol,[37] the CCSD(T), QCISD(T), and BD(T) values are overestimated, whereas the difference between the B3LYP/AE value and the experimental value decreases and the B3LYP/ECP(S) result turns out

TABLE 3: Relative Energies (in kcal/mol) of the Lowest Electronic Terms of Fe Atom (^{5}D and ^{5}F) and Fe$^+$ Cation Calculated at Various Computational Levels[a]

	UMP2	UMP4	QCISD(T)	CCSD(T)	BD(T)	B3LYP	exptl
Fe(^{5}D−^{5}F)	12.2[b] (16.4)[c]	17.9[d]	27.5	27.8 (26.1)[c]	20.3	13.7 (6.8)[c]	20.1[e]
Fe$^+$(^{6}D−^{4}F)	8.9[f] (4.2)[c] [3.1][g]	12.7[h] [5.1]	17.6 [6.9]	17.7 (8.3)[c] [7.1]	17.6 [7.1]	3.6 (−3.8)[c,i] [−4.2]	5.8[e]

[a] Calculated using the ECP(S)[23a] and the (8s7p6d2f)/[6s5p4d2f] valence basis set.[23b] [b] 12.5 kcal/mol at the PMP2/ECP(S) level. Calculations[16] at the MP2 level with Hay−Wadt ECP (ECP(H−W))[35] and a TZ-quality valence basis set gave 17.7 kcal/mol. [c] Values given in parentheses were obtained in all-electron calculations[6b] using the (14s11p6d1f)/[8s6p4d1f] basis set. [d] 24.8 kcal/mol at the MP4/ECP(H−W)/TZ level.[16] [e] *j*-averaged values[36] taken from ref 37. [f] 8.2 kcal/mol at the PMP2/ECP(S)/6s5p4d2f] level. MP2/ECP(H−W)/TZ calculations[16] led to a value of 1.8 kcal/mol. [g] The Fe$^+$(^{6}D−^{4}F) excitation energy calculated using the WHext basis set[39,40] is given in square brackets. [h] 4.9 kcal/mol at the MP4/ECP(H−W)/TZ level.[16] [i] B3LYP/ECP(S) calculations with the (8s7p6d)/[6s5p3d] basis set give the Fe$^+$(^{6}D−^{4}F) energy of 9.2 kcal/mol.[7b] The B3LYP/ECP(H−W) calculations yield a negative value (varying from −5.5[7b] to −8.5[7a] kcal/mol depending on the valence basis set contraction) for this excitation energy.

TABLE 4: Computational Results for FeH($^4\Delta$)[a]

	CI/ECP[b]	CASSCF/CI[c]	MRCI+Q[d]	MCPF[e]	BD(T)	B3LYP/ECP(S)	Exptl.[f]
r(Fe−H) (Å)	1.578 (1.718)	1.591 (1.704)	1.564 (1.692)	1.563 (1.694)	1.600 (1.685)	1.577 (1.683)	1.61 (1.77 ± 0.06)
ω (cm^{-1})	1701 (1564)	1641 (1554)	1744 (1638)	1821 (1583)	1755 (1932)	1715 (1546)	1827
D_e (kcal/mol)	35.4 (28.9)	72.87 (44.97)		38.0 (41.5)	38.21 (38.36)	34.7 (37.5)	
D_0 (kcal/mol)					35.7 (35.60)	32.3 (35.3)	36.6 ± 2.0[g]

[a] Data for the $^6\Delta$ state are shown in parentheses. [b] Calculations[43] using the [3s2p3d1f] basis set and ECP for Fe taken from ref 44. [c] The energies (including the effect of Davidson's correction) given in ref 45 were used in a parabolic fit to obtain the r_e and ω_e values; see ref 46 for details. [d] Reference 47. [e] [9s8p5d2f/4s3p2d] basis set.[46] [f] Experimental data on the r_e and ω_e values were taken from ref 41b for the $^6\Delta$ state and from ref 48 for the $^4\Delta$ state. [g] Experimental estimates for Fe−H bond energy vary from 43.97 to 26.05 kcal/mol.[49] The average FeH bond energy (D_{298} = 37.5 ± 2.0 kcal/mol) given in ref 49 was adjusted to 0 K value by subtracting 0.88 kcal/mol ((3/2)RT at 298 K).

to provide the closest agreement with experiment. However, as the ECP(S) is a quasi-relativistic pseudopotential, it is doubtful whether inclusion of such relativistic corrections is justified.

The B3LYP/ECP(S) results found for the ^{6}D−^{4}F excitation energy of Fe cation are quite satisfactory. While the B3LYP/AE calculations[6b] give rise to a negative value of −3.8 kcal/mol, the B3LYP/ECP(S) scheme leads to a value of 3.6 kcal/mol, which is remarkably close to the experimental energy of 5.8 kcal/mol. This agreement between the B3LYP/ECP and the experimental values for the ^{6}D−^{4}F excitation energy for Fe$^+$, in contrast to a qualitative disagreement in the case of the B3LYP/AE value,[6b] is of a particular importance since it does not lead to a significant error in calculated energies of the dissociation leading to Fe$^+$ cation, whereas the error in the B3LYP/AE ^{6}D−^{4}F excitation energy gives rise to an error of 9.6 kcal/mol in the dissociation energies.[6b,38] Calculations of the ^{6}D−^{4}F excitation energy at the UMP4, QCISD(T), CCSD(T), and BD(T) levels of theory using the ECP(S) give overestimated values (Table 3). The MCPF/AE (modified coupled-pair functional) and CCSD(T)/AE values are 10.4 and 8.3 kcal/mol, respectively.[6b] The B3LYP calculations using the Hay−Wadt ECP (ECP(H−W))[35] and a (5s5p3d)/[3s4p2d] valence basis set lead to a qualitatively incorrect value (−5.5 kcal/mol) for the Fe$^+$(^{6}D−^{4}F) excitation energy.[7b] We also calculated the Fe$^+$(^{6}D−^{4}F) excitation energy using the all-electron Wachters basis set[39] augmented with diffuse s and d functions as well as f polarization functions, (15s11p8d3f)/[9s6p3d1f].[40] This basis set is denoted as WHext. The Fe$^+$(^{6}D−^{4}F) excitation energy calculated with this basis set at the MP2, MP4, QCISD(T), CCSD(T), BD(T), and B3LYP levels of theory are from 6 to 10 kcal/mol lower than the excitation energy computed using the ECP(S) and the valence basis set described above (Table 3). At the B3LYP/WHext level, this energy is negative, in contrast to the experimental value of 5.8 kcal/mol.

The ^{5}D(d^{6}s^2)−^{6}D(d^{6}s^1) ionization energy of Fe calculated at the B3LYP/ECP(S) level is 8.15 eV. This value is close to the experimental result of 7.87 eV.[31] ACPF/ECP(S) calculations give 7.75 eV,[23c] whereas the calculated ionization energy is 7.41 eV at the PMP3/ECP(H-W)/DZ level.[34b]

Iron Hydride and Its Cation. According to the experimental data,[41a] the $^4\Delta$ state of FeH is the ground state.[41a] Photodetachment experiments[41b] indicate the $^6\Delta$ state to be 5.5 kcal/mol higher in energy. However, most calculations show the $^6\Delta$ state to be lower in energy, and very high levels of theory are required to get accurate state separation energies for FeH (e.g., MRCI+Q calculations with the MCPF correction for the 3s3p correlation).[42] The B3LYP/ECP(S) calculations predict the $^6\Delta$ state to be 2.8 kcal/mol lower in energy than the $^4\Delta$ state. The MCPF calculation with the [9s8p5d2f/4s3p2d] basis set also favors the $^6\Delta$ state by 3.5 kcal/mol.[43] The Fe−H bonding energies (D_e) calculated for the $^4\Delta$ and $^6\Delta$ states agree with the data of other calculations (Table 4). The corresponding D_0 values calculated for the $^4\Delta$ state at the B3LYP/ECP(S) (32.3 kcal/mol) and BD(T)/ECP(S) (35.7 kcal/mol) levels are close to the experimental estimate of 36.6 ± 2.0 kcal/mol (Table 4). The Fe−H bond length and harmonic frequencies calculated at the B3LYP/ECP(S) level are in acceptable agreement with the experimental values and close to the results of MRCI+Q[42] and BD(T)/ECP(S) calculations.

The B3LYP/ECP(S) bond dissociation energy for FeH$^+$($^5\Delta$), D(Fe$^+$−H), is 55.7 kcal/mol. The experimental D_0 value[49] (converted from 298 to 0 K) is 48.8 ± 1.4 kcal/mol. MCPF calculations give D_0(Fe$^+$−H) = 52.3 kcal/mol.[42] All-electron calculations using the B3LYP functional and Wachters basis set[39] for Fe lead to D_0(Fe$^+$−H) = 61 kcal/mol,[7c] whereas the B3LYP/AE calculations with the augmented Wachters basis set, (14s11p6d1f/[8s6p4d1f],[6d] give D_0 = 59.0 kcal/mol. For the ground $^5\Delta$ state of FeH$^+$, the r_e and ω_e values calculated at the B3LYP/ECP(S) level are 1.565 Å and 1856 cm^{-1}. These values are close to those obtained at the MCPF level (1.597 Å and 1817 cm^{-1}).[51]

The proton affinity of Fe ($FeH^+ \rightarrow Fe + H^+$) was calculated at the B3LYP/ECP(S) level to be 183.7 kcal/mol at 298 K (182.8 kcal/mol at 0 K). This is in good agreement with the experimental PA$_{298}$(Fe) value of 181.2 ± 1.4 kcal/mol.[49]

Iron Dihydride and Its Cation. Experimental data on FeH$_2$

indicate that this molecule has a linear geometry in the $^5\Delta_g$ ground state.[52] The B3LYP/ECP(S) calculated Fe−H bond length (1.647 Å) is closer to the experimental value[52] of 1.665 Å than the bond length calculated at the CI/CASSCF (1.746 Å)[53a] and CIPSI (1.70 Å)[53b] levels of theory. The antisymmetric stretching vibration calculated using B3LYP/ECP(S) is 1639 cm^{-1}, which is in good agreement with the experimental value of 1675 cm^{-1} determined in the gas-phase spectroscopic study of FeH_2.[52] There are no direct experimental estimates of the D_e(HFe−H) or D_0(HFe−H) for FeH_2 to date. The interpretation of the data of Halle et al.,[54] which was suggested by Armentrout and Sunderlin,[49a] leads to the $D_0(\text{HFe−H}) > 66.7 \pm 2$ kcal/mol. This is a very large bond strength as compared with M−H bonds in other metal hydrides.[49a] The B3LYP/ECP(S) calculations give the D_0(HFe−H) value of 69.7 kcal/mol, which agrees well with the estimate of Armentrout and Sunderlin.[49a] The B3LYP/ECP(S) calculations indicate that the $Fe + H_2 \rightarrow FeH_2$ reaction is almost thermoneutral. (The reaction energy and enthalpy are 2.2 and 0.4 kcal/mol, respectively.)

For the FeH_2^+ cation having a C_{2v} structure ($R(\text{H−H}) = 0.811$ Å, $R(\text{Fe−H}) = 1.704$ Å, $\angle\text{HFeH} = 27.5°$) in the ground ($^4A_2$) state, the B3LYP/ECP(S) calculated $D_0(Fe^+{-}H_2)$ value is 9.8 kcal/mol, which agrees better with the experimental value of 5 kcal/mol[31] than the B3LYP/AE value of 19 kcal/mol.[7c]

Iron Oxide and Its Cation. The highest level calculations on FeO to date (IC-ACPF/[7s 6p 4d 3f 2g]) leads to a bond dissociation energy for FeO of 84.2 kcal/mol.[55] The experimental estimates vary from 92.9 ± 3.0[56] to 95.9 ± 1.8 kcal/mol.[57] Our B3LYP/ECP(S) calculations of FeO give D_e and D_o values of 93.0 and 91.7 kcal/mol, respectively. Calculations at the BD(T)/AE level[58] using the extended Wachters basis set lead to D_e and D_o values of 89.4 and 88.3 kcal/mol, respectively. The B3LYP/ECP(S) calculated Fe−O bond length (1.614 Å) is close to the experimental value of 1.616 Å.[59] The B3LYP/AE calculations[6h] using the Wachters basis set (augmented with diffuse d and f polarization functions; (15s12p6d1f)/[9s7p4d1f]) gives $R(\text{Fe−O}) = 1.611$ Å. The Fe−O bond length calculated at the CASSCF level is 1.609 Å.[55] The harmonic frequency was calculated at the B3LYP/ECP(S) level to be 887 cm^{-1} (869 cm^{-1} using a scaling factor of 0.98). This is close to the experimental estimate[60] of 880 cm^{-1} and to a value of 885 cm^{-1} obtained by recent ICACPF/CASSCF calculations.[55] The B3LYP/AE calculations led to a 903 cm^{-1} fundamental.[6h] The ionization energy of FeO calculated at the B3LYP/ECP(S) level (8.9 eV) is in excellent agreement with the experimental value[31,61] of 8.9 ± 0.1 eV. This is apparently a fortuitous agreement.[62]

The enthalpy of formation of FeO calculated at the B3LYP/ECP(S) level agrees with the experimental data[31] (Table 5). The B3LYP/ECP(S) calculated proton affinity of FeO is 222.2 kcal/mol at 0 K. This is rather close to the experimental estimate of PA_0(FeO) which is 211 ± 5 kcal/mol.[31]

According to higher level calculations,[64] the ground state of FeO^+ is the $^6\Sigma^+$ state having the dissociation energy, $D_0(Fe^+{-}O)$, of 81.0 kcal/mol (at the CASPT2N level with BSSE corrections). This is in excellent agreement with the recent experimental D_o value of 81.4 ± 1.4 kcal/mol.[65] (Another experimental estimate for D_o(Fe−O) is 68 ± 5 kcal/mol.[66]) The MRCI+D calculations give a D_e value of 74.6 kcal/mol.[64] The D_e and D_o values for FeO^+ calculated at the B3LYP/ECP(S) level are 75.8 and 74.7 kcal/mol, respectively. The Fe−O bond length in FeO^+ calculated at this level (1.640 Å) is close to the value of 1.643 Å found by the CASPT2N calculations.[64] The B3LYP/ECP(S) calculated enthalpy of formation for FeO^+ is in reasonable agreement with the experimental value (Table 5).

TABLE 5: B3LYP/ECP(S) Calculated and Experimental Gas Phase Enthalpies of Formation (in kcal/mol)[a]

species	$\Delta H_{f\,o}$(calc)	$\Delta H_{f\,o}$(exptl)	Δ[b]
$FeO(^5\Delta)$	66.2[c]	60.0 ± 5	−6.2
$FeO^+ (^6\Sigma^+)$	271.3[c]	265.3	−6.0
$FeOH(^6A')$	33.8	31.9 ± 4	−1.9
$FeOH^+(^5A'')$	210.7	214[d]	+3.3[d]
$FeS(^5\Delta)$	94.7	88.6 ± 3.9	−6.1
$FeF(^6\Delta)$	14.3	11.4 ± 5.0	−2.9
$FeCl(^6\Delta)$	54.0	59.7 ± 21	+4.7
$FeCH^+(^3\Delta)$	335.6	322 ± 7	−13.6
$FeCH_2^+(^4B_2)$	285.6	292	+6.4

[a] Experimental $\Delta H_{f\,o}$ values are taken from refs 30 and 31 unless stated otherwise. [b] $\Delta = \Delta H_{f\,o}(\text{exptl}) - \Delta H_{f\,o}(\text{calc})$. [c] B3LYP/ECP(S) calculated $\Delta H_{f\,298}$(FeO) value is 66.1 kcal/mol. This value is close to the experimental estimate[30] of 60.0 ± 5 kcal/mol. [d] Recent experimental results[68] indicate that the $\Delta H_f(FeOH^+)$ value is lower than the value given in ref 31.

TABLE 6: B3LYP/ECP(S) Calculated and Experimental Gas Phase Bond Dissociation Energies (in kcal/mol)[a]

bond	D_0(calc)	D_0(exptl)	D_0(exptl) − D_0(calc)
$Fe^+{-}H$	55.7	48.4 ± 1.4[b]	−7.3
$Fe^+{-}H_2$	9.8	5.0	−4.8
Fe−O	91.7	92.9 ± 3.0	+1.2
$Fe^+{-}O$	74.7	81.4 ± 1.4	+6.7
Fe−OH	72.7	76.9 ± 4[c]	+4.2
$Fe^+{-}OH$	83.8	73−87	−3.8[i]
Fe−S	69.9	76.3	+6.4
Fe−F	103.2	107 ± 5	+3.8
$Fe^+{-}F$	98.6	95.8[d]	−2.8
Fe−Cl	73.5	77.9 ± 3.4[e]	+4.4
$Fe^+{-}Cl$	76.2	83.9[d]	+7.7
$Fe^+{-}CH$	91.5	99.5 ± 7	+8.0
$Fe^+{-}CH_2$	79.7	82 ± 5[f]	+2.3
$Fe^+{-}C_2H_6$	19.9	17.9 ± 3[g]	−2.0
$Fe^+{-}CO$	27.1	31.3 ± 8[h]	+4.2

[a] Experimental values are taken from ref 31 unless stated otherwise. [b] Reference 49. [c] Reference 56. [d] Reference 66. [e] Reference 84. [f] Reference 70. [g] Reference 77. [h] Reference 83. [i] An average D_0 $(Fe^+{-}OH)$ value of 80 kcal/mol was taken as the experimental estimate.

Iron Monohydroxide and Its Cation. The B3LYP/ECP(S) calculations show that FeOH has the $^6A'$ ground state. The quartet ($^4A'$) state is 8.7 kcal/mol higher in energy at the B3LYP level using the 6-311G(d,p) basis set for oxygen and hydrogen and the (8s7p6d)/[6s5p3d] valence basis set for iron, respectively. The B3LYP/ECP(S) calculated D_o(Fe−OH) (72.7 kcal/mol, $D_e = 74.3$ kcal/mol) and ionization energy (7.66 eV) agree well with the experimental values of 76.9 ± 4 kcal/mol and 7.9 ± 0.2 eV, respectively.[56]

The bond dissociation energy of $Fe^+{-}OH$ ($^5A''$) calculated at the B3LYP/ECP(S) level is 83.8 kcal/mol ($D_e = 85.6$ kcal/mol) (Table 6). This value lies within a range of the experimental estimates which vary from 73 and 79 to 87 kcal/mol (for details, see refs 65−67). The B3LYP/ECP(S) calculated enthalpy of formation for $FeOH^+$ is 210.7 kcal/mol at 0 K (Table 5). This value is only 3.3 kcal/mol smaller than the experimental estimate of $\Delta H_{f\,0}(FeOH^+)$, and recent experimental studies[68] indicate that the $\Delta H_{f\,0}(FeOH^+)$ value is somewhat lower than that given in ref 31.

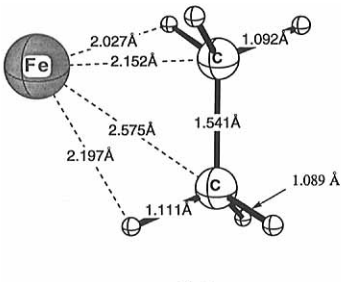
Iron Sulfide. The B3LYP calculated bond length (2.045 Å) and the harmonic vibrational frequency (502 cm^{-1}) are close to the ICACPF/CASSCF values[55] of 2.024 Å and 521 cm^{-1}. The Fe−S bond dissociation energies, D_e and D_o, are 70.56 and 69.87 kcal/mol. The D_o value for $FeS(^5\Delta)$ calculated at the B3LYP/ECP(S) level agrees better with the experimental value[66] of 76.3 kcal/mol than a value of 64.6 kcal/mol obtained in the ICACPF/CASSCF calculations.[55] The BD(T)/AE calculations with the extended Wachters basis set give R(Fe−S) = 2.041 Å, D_e = 68.61, and D_o = 67.83 kcal/mol.[58] The enthalpy of formation for FeS ($\Delta H_{f\,0}$) calculated using B3LYP/ECP(S) is 94.7 kcal/mol (Table 5). This is in acceptable agreement with the experimental estimate of 88.6 ± 3.9 kcal/mol.[30]

$FeCH_n$ (n = 1 and 2) and Their Cations. The dissociation energy for FeCH($^2\Delta$) was calculated to be 68.4 kcal/mol (D_e = 71.1 kcal/mol) at the B3LYP/ECP(S) level. The B3LYP/ECP(S) Fe−C bond length in FeCH (1.739 Å) is shorter than that calculated at the MP2/ECP(H-W)/TZ level (1.904 Å).[16] For $FeCH^+$($^3\Delta$) the D_e, D_o, and $\Delta H_{f\,0}$ values calculated at the B3LYP/ECP(S) level are 94.6, 91.5, and 335.6 kcal/mol, respectively. While the calculated Fe^+−CH bond dissociation energy (D_o) is slightly smaller than the experimental estimate of 99.5 ± 7 kcal/mol,[70,71] the $\Delta H_{f\,0}$ value displays a larger deviation (13.6 kcal/mol) from the experimental value of 322 ± 7 kcal/mol, respectively.[70] The PMP4/ECP(H−W)/TZ//MP2/ECP(H−W)/TZ calculations[16] led to an underestimated value of D_o (78.1 kcal/mol) for Fe^+−CH. The Fe−C bond length in $FeCH^+$ calculated at this level is 1.813 Å,[16] whereas the B3LYP/ECP(S) geometry optimization led to a 0.074 Å shorter bond length.

B3LYP/ECP(S) calculations give D_e and D_o values for Fe−CH_2($^3B_2$) which are 59.1 and 56.7 kcal/mol, respectively. Similar to the D_e and D_o values for Fe−CH, these bond dissociation energies for iron methylene are larger than those calculated at the PMP4/ECP(H−W)/TZ level (34.8 and 32.6 kcal/mol, respectively). Our all-electron calculations[58] at the QCISD(T)/MP2 level using the Wachters basis set[39] augmented by two 4p functions, a diffuse d function, and diffuse s and three f functions also lead to lower D_e (48.8 kcal/mol) and D_o (46.4 kcal/mol) values. To the best of our knowledge, there are no experimental estimates for the Fe−CH_2 bond energy to date. The IR spectrum of iron methylene isolated in argon matrix has been reported.[72] The B3LYP/ECP(S) calculated the Fe−C stretching frequency of 567 cm^{-1} (scaled with 0.98) is close to the experimental value[72] of 623.6 cm^{-1}, and it is not clear to what extent matrix effects are amenable for this difference.

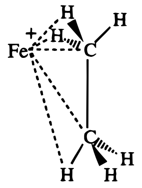
In contrast to $FeCH_2$, many studies, both experimental[46b,70,73] and theoretical,[6c,16,74,75] have been carried out on $FeCH_2^+$. The Fe−C bond length for the $^4B_1$ ground state of $FeCH_2^+$ was calculated to be 1.817 and 1.857 Å at the MCPF and B3LYP/AE levels of theory.[6c] The geometry optimization of $FeCH_2^+$ at the MP2 level using the Hay−Wadt ECP led to a longer value (1.889 Å) for the Fe−C bond length.[16] Our B3LYP/ECP(S) calculations resulted in the Fe−C bond length of 1.850 Å. Calculations of the Fe^+−CH_2 bond dissociation energy (D_e) gave 71.5 (ICAPF),[74a] 63.4 (MCPF),[74b] 59.1 (CCSD),[74a] and 70.9 kcal/mol (CCSD(T)).[74a] The D_o energy was calculated to be 68 kcal/mol at the MR-SDCI-CASSCF level of theory,[75] 74 ± 5 kcal/mol at the ICAPF level,[74a,76] 61.6 kcal/mol at the PMP4/ECP(H-W)/TZ level,[16] and 87.3 kcal/mol at the B3LYP level with an all-electron (14s11p6d3f)/[8s7p4d2f] basis set.[6c] The B3LYP/AE calculations using a DZP-type basis set give D_o(Fe^+−CH_2) = 79.2 kcal/mol.[2b] Our B3LYP/ECP(S) calculations on $FeCH_2^+$($^4B_2$) lead to the D_e and D_o values of 82.6 and 79.7 kcal/mol, respectively. This D_o value is in good agreement with the experimental estimates of 82 ± 5[70] and 81.5 ± 4 kcal/mol.[73b] We also calculated the enthalpy of formation for $FeCH_2^+$. The obtained $\Delta H_{f\,0}$ value is 285.6 kcal/mol, which is in a reasonably good agreement with the experimental $\Delta H_{f\,0}$ value[31] of 292 kcal/mol (Table 5).

Complex of Iron Cation with Ethane. In contrast to the above $FeCH^+$ and $FeCH_2^+$ complexes, the $FeC_2H_6^+$ complex exemplifies a relatively weak complex with the experimental bond dissociation energy (D_o(Fe^+−C_2H_6)) of only 17.9 ± 3 kcal/mol.[77,78] We calculated various geometries of Fe^+−C_2H_6 complexes, **1**−**4**. The C_s structure of the $^4A''$ state (**1a**) is the lowest in energy. The ethane moiety in **1a** maintains the staggered conformation of ethane, and the Fe−H distances are 2.027 and 2.197 Å (Figure 1), whereas the C_{2v} structure **2a** with shorter Fe−H distances (1.842 Å) but longer Fe−C distances (2.366 Å) than those in **1a** is not a minimum. The charge on the iron calculated using the natural population analysis (NPA)[79] at the UHF/6-311+G(3df,2p)/ECP(S) level is 0.954. This value, which is very close to that calculated using the Wachters basis set augmented with diffuse p and d functions (0.95),[80] shows that the interaction between the iron and ethane is mainly electrostatic. We did not consider the $H_3CFeCH_3^+$ structure which is higher in energy than **1a** as shown by recent calculations at the B3LYP/AE[80] and MCPF[81] levels of theory.

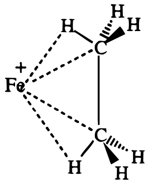


1a C_s

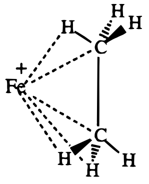
Figure 1. The C-C and C-H bond lengths as well as the Fe-H and Fe-C distances in the Fe^+-C_2H_6 C_s structure **1a** optimized at the B3LYP/ECP(S) level.



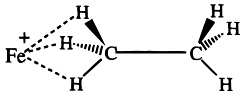
1 C_s



2 C_{2v}



3 C_2



4 C_{3v}

(**a** = quartet state, **b** - sextet state)

The B3LYP/ECP(S) calculated bond dissociation energy, D_o(Fe^+−C_2H_6), for the lowest energy structure **1a** is 19.9 kcal/mol (Table 7). This value agrees with the experimental estimate of 17.9 ± 3 kcal/mol,[77,78] in contrast to the B3LYP/AE calculated value of 27 kcal/mol.[80] As noted above, the B3LYP/ECP(S) calculations reproduce the Fe^+(^6D−^4F) excitation energy reasonably well, whereas the B3LYP/AE calculations lead to a qualitatively incorrect result (Table 3). This resulted in an overestimated D_o(Fe^+−C_2H_6) value calculated at the B3LYP/AE level.

$FeCO^+$. Computational results for $FeCO^+$ obtained at various levels of theory are presented in Table 7. As seen from these data, B3LYP/ECP(S) calculations provide values that are in general agreement with the results of higher level calculations. The Fe^+−CO bond dissociation energy (D_o) is 27.1 kcal/mol at the B3LYP/ECP(S) level. This value is close to the best

TABLE 7: Computational Results for $FeCO^+$ ($^4\Sigma^-$)[a]

	UHF	UMP2	CCSD(T)	MCPF	B3LYP
r(Fe−C) (Å)	2.139	1.880	1.910	1.922	1.873 (1.887)[b]
r(C−O) (Å)	1.098	1.145	1.140	1.136	1.126 (1.129)
ν(bend) (cm^{-1})	264	321			314 (319)
ν(Fe−CO) (cm^{-1})	243	405			425 (423)
ν(C−O) (cm^{-1})	2522	2153			2237 (2225)
D_e (kcal/mol)	−29.0	26.6	23.1	20.0	28.6 (42.3)

[a] The data of all-electron calculations at the UHF, UMP2, CCSD(T), MCPF, and B3LYP levels of theory were taken from ref 6c. [b] Results of the all-electron B3LYP calculations[6c] using the (14s11p6d1f)/[8s6p4d1f}basis set for Fe are given in parentheses.

TABLE 8: B3LYP/ECP(S) Calculated and Experimental Ionization Energies (eV)[a]

species	IE(calc)	IE(exptl)	IE(exptl) − IE(calc)
Fe	8.15	7.87	−0.28
FeO	8.90	8.9 ± 0.16	0.0
FeOH	7.66	7.9 ± 0.2	0.24
FeCl	8.01	≤8.08 ± 0.10[b]	0.07

[a] Experimental values are taken from ref 31. [b] Reference 84.

theoretical value[82] of 30.7 kcal/mol and the experimental estimate[83] of 31.3 ± 1.8 kcal/mol (Table 6).

Iron Fluoride, Iron Chloride, and Their Cations. The bond dissociation energies of FeX($^6\Delta$) and FeX^+($^5\Delta$) (X = F and Cl) and the ionization energy of FeCl calculated using the B3LYP/ECP(S) scheme are given in Tables 6 and 8. These values agree well with experimental estimates. While the B3LYP/AE and QCISD(T) calculations using the Wachters basis set give the D_o(Fe−Cl) values of 81.57 and 81.8 kcal/mol, respectively,[40] the B3LYP/ECP(S) calculations lead to D_o(Fe−Cl) = 73.5 kcal/mol. All these calculated D_o values demonstrate good agreement with the experimental estimate of 77.9 ± 3.4 kcal/mol.[84] The D_o(Fe^+−Cl) values calculated at the QCISD(T)//QCISD and B3LYP//B3LYP levels using augmented Wachters basis sets (80.3 and 83.8 kcal/mol) show better agreement with the experimental estimate (83.9 kcal/mol)[66] than the B3LYP/ECP(S) value of 76.2 kcal/mol (Table 6). The B3LYP/ECP(S) calculated adiabatic ionization energy (IE) of FeCl is 8.01 eV (Table 8), which is closer to the experimental estimate of ≤8.08 ± 0.10 eV[84] than the QCISD(T) and B3LYP/AE calculated IE values of 7.89 and 7.85 eV, respectively.[40] The B3LYP $\Delta H_{f\,0}$ values for FeF and FeCl agree with the experimental data (Table 5), although it should be noted that the $\Delta H_{f\,0}$(FeCl) value given in ref 30 is an indirect estimate (with an uncertainty of ± 21 kcal/mol), and our calculations at the QCISD(T)/AE level give a smaller ΔH_f(FeCl) value.[40]

It is notable that while the bond strength decreases from Fe−F to Fe^+−F, an opposite ordering is found for the D_o(Fe−Cl) and D_o(Fe^+−Cl) values (Table 6), although the Fe−X bond lengths (X = F and Cl) are shorter in the cations (1.711 (X = F) and 2.079 Å (X = Cl)) than those in the corresponding neutral molecules (1.804 (X = F) and 2.234 Å (X = Cl)). The Fe−F bond length in FeF optimized at the B3LYP/ECP(S) level demonstrates good agreement with the experimental estimate of the r_e(Fe−F) = 1.7914 Å.[85] The Fe−Cl bond length in FeCl calculated using the B3LYP/ECP(S) scheme is slightly longer than the values found at the QCISD/AE (2.179 Å) and B3LYP/AE (2.196 Å) levels of theory.[40] The harmonic frequency calculated for FeF at the B3LYP/ECP(S) level (638 cm^{-1}, the scaled value is 625 cm^{-1}) is close to the experimental value[30] of 630 cm^{-1}. For FeCl, however, the B3LYP/ECP(S) frequency (370 cm^{-1}, the scaled value is 362 cm^{-1}) is smaller than the experimental estimate (404.9 cm^{-1})[30] and the MP2/AE value of 409 cm^{-1} (unscaled).[40]

4. Conclusions

Our calculations of iron-containing molecules and ions with various types of bonding, which were carried out using the B3LYP/ECP(S) computational scheme, lead to the following conclusions:

(1) B3LYP/ECP(S) calculations of iron-containing species are capable of providing reliable results. The dissociation energies calculated for iron-containing species with various bonding with experimental estimates of the bond strength varying from 5.0 (Fe^+−H_2) to 99.5 kcal/mol (Fe^+-−H), i.e., within a range of 95 kcal/mol (Table 6), do not reveal any systematic trends in the errors. The average absolute deviation is 4.6 kcal/mol. The largest deviation form the experimental D_o value is +8.0 kcal/mol for Fe^+−CH. This experimental estimate, however, has an uncertainty of ±7 kcal/mol.

(2) The B3LYP/ECP(S) calculated enthalpies of formation (Table 5) have an average absolute deviation of 5.7 kcal/mol with the largest deviation of 14 ± 7 kcal/mol of the experimental $\Delta H_{f\,0}$ value in the case of $FeCH^+$.

(3) The ionization energies calculated using the B3LYP/ECP(S) scheme (Table 8) demonstrate acceptable agreement with the experimental values.

(4) Geometries and harmonic frequencies calculated using the B3LYP/ECP(S) scheme are generally in good agreement with the available experimental data or with results of higher level calculations.

(5) While in some cases the data obtained are even in better agreement with the experimental values than the results of higher level all-electron calculations, the performance of the B3LYP/ECP(S) approach should not be overestimated. We do not consider the set of iron-containing species used in our study as a comprehensive set representing all types of Fe−L bonding. Therefore, it is possible that larger deviations can be found in B3LYP/ECP(S) calculations of other iron compounds. It is not clear for now whether reliable results can be found in B3LYP/ECP(S) calculations of species with iron−iron bonding and species containing other first-row transition metals as well the second- and third-row transition metals. These studies are in progress.

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References and Notes

(1) (a) Salahub, D. R.; Zerner, M. C., Eds. *The Challenge of d and f Electrons—Theory and Computation*; ACS Symposium Series 394; American Chemical Society: Washington, DC, 1989. (b) Siegbahn, P. E. M. *Adv. Chem. Phys.* **1996**, *93*, 333.

(2) (a) Labanowski, J. K., Andzelm, J. W., Eds. *Density Functional Methods in Chemistry*; Springer: New York, 1991. (b) Ellis, D. E., Ed. *Density Functional Theory of Molecules, Clusters, and Solids*; Kluwer: Dordrecht, 1995.

(3) (a) Becke, A. D. *Phys. Rev. A* **1988**, *37*, 785. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B41*, 785.

(4) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Stevens, P. J.; Devlin, F. J.; Chablowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *80*, 11623.

(5) (a) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651. (b) Ziegler, T.; Li, J. *Can. J. Chem.* **1994**, *72*, 783. (c) Li, J.; Schreckenbach, G.; Ziegler, T. *J. Phys. Chem.* **1994**, *98*, 4838.

(6) (a) Ricca, A.; Bauschlicher, C. W. *J. Phys. Chem.* **1994**, *98*, 12899. (b) Ricca, A.; Bauschlicher, C. W. *Theor. Chim. Acta* **1995**, *92*, 123. (c) Ricca, A.; Bauschlicher, C. W. *Chem. Phys. Lett.* **1995**, *245*, 150. (d) Bauschlicher, C. W.; Sodupe, M. *Chem. Phys. Lett.* **1995**, *240*, 526. (e) Xu, Y. C.; Lee, S. A.; Freiser, B. S.; Bauschlicher, C. W. *J. Am. Chem. Soc.* **1995**, *117*, 5413. (f) Bauschlicher, C. W.; Maitre, P. *J. Phys. Chem.*

1995, *99*, 3444. (g) Maitre, P.; Bauschlicher, C. W. *J. Phys. Chem.* **1995**, *99*, 6836. (h) Chertihin, G. V.; Saffel, W.; Yustein, J. T.; Andrews, L.; Nuerock, M.; Ricca, A.; Bauschlicher, C. W. *J. Phys. Chem.* **1996**, *100*, 5261.

(7) (a) Holthausen, M. C.; Heinemann, C.; Cornehl, H.; Koch, W.; Schwarz, H. *J. Chem. Phys.* **1995**, *102*, 4931. (b) Holhausen, M. C.; Mohr, M.; Koch, W. *Chem. Phys. Lett.* **1995**, *240*, 245. (c) Holthausen, M. C.; Fiedler, A.; Schwarz, H.; Koch, W. *Angew. Chem.* **1995**, *107*, 2430. (d) Schröder, D.; Fiedler, A.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1994**, *134*, 239. (e) Dargel, T. K.; Koch, W. *J. Chem. Soc., Perkin Trans. 2* **1996**, 877.

(8) (a) Russo, T. V.; Martin, R. L.; Hay, P. J. *J. Chem. Phys.* **1994**, *101*, 7729. (b) Fournier, R. *J. Chem. Phys.* **1993**, *99*, 1801. (c) Castro, M.; Salahub, D. R.; Fournier, R. *J. Chem. Phys.* **1994**, *100*, 8233. (d) Wu, Y.-D.; Lai, D. K. W. *J. Am. Chem. Soc.* **1995**, *117*, 11327. (e) Harada, M.; Dexpert, H. *J. Phys. Chem.* **1996**, *100*, 565. (f) Hack, M. D.; Maclagan, R. G. A. R.; Scuseria, G. E.; Gordon, M. S. *J. Chem. Phys.* **1996**, *104*, 6628. (g) Wüllen, C. V. *Int. J. Quantum Chem.* **1996**, *58*, 147. (h) Murray, C. W.; Handy, N. C.; Amos, R. D. *J. Chem. Phys.* **1993**, *98*, 7145. (i) Tozer, D. J. *J. Chem. Phys.* **1996**, *104*, 4166. (j) Lee, T. J. *Chem. Phys. Lett.* **1990**, *169*, 529. (k) Cramer, C. J.; Worthington, S. E. *J. Phys. Chem.* **1995**, *99*, 1462. (l) It appears, however, that DFT methods cannot provide reliable results for species having degenerate electronic states, for example, for trimethylenemethane. See: Cramer, C. J.; Smith, B. A. *J. Phys. Chem.* **1996**, *100*, 9664.

(9) (a) Bauschlicher, C. W.; Partridge, H. *Chem. Phys. Lett.* **1995**, *240*, 533. (b) Bauschlicher, C. W.; Partridge, H. *J. Chem. Phys.* **1995**, *103*, 1788. (c) Hertwig, R. H.; Koch, W. *J. Comput. Chem.* **1995**, *16*, 576. (d) Mebel, A. M.; Morokuma, K.; Lin, M. C. *J. Chem. Phys.* **1995**, *103*, 7414. (e) Hay, P. J. *J. Phys. Chem.* **1996**, *100*, 5. (f) Glukhovtsev, M. N.; Bach, R. D.; Laiter, S. *J. Phys. Chem.* **1996**, *100*, 10952.

(10) Smith, B. J.; Radom, L. *Chem. Phys. Lett.* **1994**, *231*, 345.

(11) Rauhut, G.; Pulay, P. *J. Phys. Chem.* **1995**, *99*, 3093.

(12) (a) Krauss, M.; Stevens, W. J. *Annu. Rev. Phys. Chem.* **1984**, *35*, 357. (b) Christiansen, P. A.; Ermler, W. C.; Pitzer, K. S. *Annu. Rev. Phys. Chem.* **1985**, *36*, 407. (c) Gropen, O. In *Methods in Computational Chemistry*; Wilson, S., Ed.; Plenum: New York, 1988; Vol. 2, p 109.

(13) Frenking, G.; Antes, I.; Böhme, M.; Dapprich, S.; Ehlers, A. W.; Jonas, V.; Neuhaus, A.; Otto, M.; Stegmann, R.; Veldkamp, A.; Vyboishchikov, S. F. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: Weinheim, 1995; Vol. VII.

(14) (a) Pyykkö, P. *Adv. Quantum Chem.* **1978**, *11*, 353. (b) Pyykkö, P. *Acc. Chem. Res.* **1979**, *12*, 276. (c) Pitzer, K. S. *Acc. Chem. Res.* **1979**, *12*, 271. (d) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563. (e) Wilson, S., Ed. *Relativistic Effects in Atoms and Molecules*; Methods in Computational Chemistry; Plenum: New York, 1989; Vol. 2.

(15) (a) Golding, R. M. *Applied Wave Mechanics*; Van Nostrand: New York, 1969. (b) Szasz, L. *The Electronic Structures of Atoms*; Wiley: New York, 1992.

(16) Veldkamp, A.; Frenking, G. *J. Comput. Chem.* **1992**, *13*, 1184.

(17) Chen, H.; Krasowski, M.; Fitzgerald, G. *J. Chem. Phys.* **1993**, *98*, 8710.

(18) Glukhovtsev, M. N.; Pross, A.; McGrath, M. P.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 1878.

(19) Salahub, D. R. In *Ab Initio Methods in Quantum Chemistry. Part II*; Lawley, K. P., Ed.; Wiley: New York, 1987; p 447.

(20) Bauschlicher, C. W.; Langhoff, S. R.; Partridge, H. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995; p 1280.

(21) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Wong, M. W.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN-94*; Gaussian Inc.: Pittsburgh, PA, 1995.

(23) (a) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, *86*, 866. (b) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, *86*, 2123. (c) Andrae, D.; Dolg, M.; Stoll, H.; Ermler, W. C. *Chem. Phys. Lett.* **1994**, *220*, 341.

(24) Russo, T. V.; Martin, R. L.; Hay, P. J. *J. Phys. Chem.* **1995**, *99*, 17085.

(25) (a) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214. (b) Schlegel, H. B. *Adv. Chem. Phys.* **1987**, *67*, 249. (c) Schlegel, H. B. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995; p 459.

(26) Handy, N. C.; Pople, J. A.; Head-Gordon, M.; Raghavachari, K.; Trucks, G. W. *Chem. Phys. Lett.* **1989**, *164*, 185.

(27) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(28) (a) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479. (b) Bartlett, R. J. *Annu. Rev. Phys. Chem.* **1981**, *32*, 359.

(29) McQuarrie, D. A. *Statistical Thermodynamics;* University Science Books: Mill Valley, CA, 1973.

(30) Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14* (Suppl. 1).

(31) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17* (Suppl. 1).

(32) Glukhovtsev, M. N.; Laiter, S. *J. Phys. Chem.* **1996**, *100*, 1569.

(33) Ervin, K. M.; Gronet, S.; Barlow, S. E.; Giles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Linenberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750.

(34) (a) McKee, M. L. *J. Am. Chem. Soc.* **1990**, *112*, 2601. (b) McKee, M. L. *J. Phys. Chem.* **1992**, *96*, 1683.

(35) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(36) Moore, C. E. *Atomic Energy Levels*; U.S. National Bureau of Standards: Washington, DC; Circ. No. 467, 1949.

(37) Raghavachari, K.; Trucks, G. W. *J. Chem. Phys.* **1989**, *91*, 1062.

(38) Holthausen, M. C.; Fiedler, A.; Schwarz, H.; Koch, W. *J. Phys. Chem.* **1996**, *100*, 6236.

(39) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033.

(40) Bach, R. D.; Shobe, D. S.; Schlegel, H. B.; Nagel, C. J. *J. Phys. Chem.* **1996**, *100*, 8770.

(41) (a) Beaton, S. P.; Evenson, K. M.; Nelis, T.; Brown, J. M. *J. Chem. Phys.* **1988**, *89*, 4446. (b) Stevens, A. E.; Feigerle, C. S.; Lineberger, W. C. *J. Chem. Phys.* **1983**, *78*, 5420.

(42) Bauschlicher, C. W.; Langhoff, S. P. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; p 103.

(43) Sodupe, M.; Lluch, J. M.; Oliva, A.; Illas, F.; Rubio, J. *J. Chem. Phys.* **1990**, *92*, 2478.

(44) Pelissier, M.; Durand, P. *Theor. Chim. Acta* **1980**, *55*, 43.

(45) Walch, S. P.; Bauschlicher, C. W. *J. Chem. Phys.* **1983**, *78*, 4597.

(46) Chong, D. P.; Langhoff, S. R.; Bauschlicher, C. W.; Walsh, S. P.; Partridge, H. *J. Chem. Phys.* **1986**, *85*, 2850.

(47) Bauschlicher, C. W. *J. Chem. Phys.* **1987**, *86*, 5591.

(48) Phillips, J. G.; Davis, S. P.; Lindgren, B.; Balfour, W. J. *Astrophys. J. Suppl. Ser.* **1987**, *65*, 721

(49) (a) Armentrout, P. B.; Sunderlin, L. S. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; pp 1−64. (b) Armentrout, P. B. In *Bonding Energetics in Organometallic Compounds*; Marks, T. J., Ed.; American Chemical Society: Washington, DC, 1990; pp 18−33.

(50) Armentrout, P. B.; Georgiadis, R. *Polyhedron* **1988**, *7*, 1573.

(51) Pettersson, L. G. M.; Bauschlicher, C. W.; Langhoff, S. R. *J. Chem. Phys.* **1987**, *87*, 481.

(52) (a) Körsgen, H.; Mürtz, P.; Lipus, K.; Urban, W.; Towle, J. P.; Brown, J. M. *J. Chem. Phys.* **1996**, *104*, 4859. For an earlier experimental study on iron dihydride, see: (b) Ozin, G. A.; McCaffrey, J. G. *J. Phys. Chem.* **1984**, *88*, 645. (c) Rubinovitz, R. L.; Nixon, E. R. *J. Phys. Chem.* **1986**, *90*, 1940. (d) Sweany, R. L. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; pp 65−101.

(53) (a) Siegbahn, P. E. M.; Blomberg, M. R. A.; Bauschlicher, C. W. *J. Chem. Phys.* **1984**, *81*, 1373. (b) Granucci, G.; Persico, M. *Chem. Phys.* **1992**, *167*, 121.

(54) Halle, L. F.; Klein, F. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 2543.

(55) Bauschlicher, C. W.; Maitre, P. *Theor. Chim. Acta* **1995**, *90*, 189.

(56) Murad, E. *J. Chem. Phys.* **1980**, *73*, 1381.

(57) (a) Smoes, S.; Drowart, J. *High Temp. Sci.* **1984**, *17*, 31. (b) Merer, A. J. *Annu. Rev. Phys. Chem.* **1989**, *40*, 407.

(58) Bach, R. D.; Glukhovtsev, M. N.; Schobe, D. S. To be published.

(59) Cheung, A. S. C.; Lee, N.; Lyyra, A. M.; Merer, A. J.; Taylor, W. W. *J. Mol. Spectrosc.* **1982**, *95*, 213.

(60) Green, D. W.; Reedy, G. T.; Kay, J. G. *J. Mol. Spectrosc.* **1979**, *78*, 257.

(61) (a) Merer, A. J. *Annu. Rev. Phys. Chem.* **1989**, *40*, 407. (b) Armentrout, P. B.; Halle, L. F.; Beachamp, J. L. *J. Chem. Phys.* **1982**, *76*, 2449.

(62) Another estimate for IE(FeO) derived from the experimental D_0-($Fe^+{-}O$)[63] is 8.64 ± 0.12 eV.

(63) Loh, S. K.; Fisher, E. R.; Lian, L.; Schultz, R. H.; Armentrout, P. B. *J. Phys. Chem.* **1989**, *93*, 3159.

(64) Fiedler, A.; Hrusák, J.; Koch, W.; Schwarz, H. *Chem. Phys. Lett.* **1993**, *211*, 242.

(65) Freiser, B. S. In *Bonding Energetics in Organometallic Compounds*; Marks, T. J., Ed.; American Chemical Society: Washington, DC, 1990; pp 55−69.

(66) Schröder, D.; Hrusák, J.; Schwarz, H. *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 1085.

(67) Schröder, D.; Schwarz, H. *Angew. Chem., Int. Ed. Engl* **1995**, *34*, 1973.

(68) See footnote 37 in: Fiedler, A.; Schröder, D.; Shaik, S.; Schwarz, H. *J. Am. Chem. Soc.* **1994**, *116*, 10734.

(69) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

(70) (a) Hettich, R. L.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 2537. (b) Other experimental estimates for the $D_o(Fe^+{-}CH)$ are 101 ± 7 and 115 ± 20 kcal/mol; see ref 65.

(71) Corrected from the experimental D_0 value at 298 K to the D_o value at 0 K; for details see ref 16.

(72) Chang, S.-C.; Kafari, Z. H.; Hauge, R. H.; Billups, W. E.; Margrave, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 1447.

(73) (a) Schultz, R. H.; Armentrout, P. B. *Organometallics* **1992**, *11*, 828. (b) Armentrout, P. B.; Sunderlin, L. S.; Fisher, E. R. *Inorg. Chem.* **1989**, *28*, 4437. (c) Haynes, C. L.; Chen, Y.-M.; Armentrout, P. B. *J. Phys. Chem.* **1996**, *100*, 111 and references therein.

(74) (a) Bauschlicher, C. W.; Partridge, H.; Sheehy, J. A.; Langhoff, S. R.; Rosi, M. *J. Phys. Chem.* **1992**, *96*, 6969. (b) Bauschlicher, C. W.; Partridge, H.; Scuseria, G. E. *J. Chem. Phys.* **1992**, *97*, 7471.

(75) Musaev, D. G.; Morokuma, K. *J. Chem. Phys.* **1994**, *101*, 10697.

(76) The $^4B_1$ and $^4B_2$ states of $FeCH_2^+$ are nearly degenerate with an energy diffrence of 0.1 kcal/mol. The $^4B_1$ state was considered for calculations of the $D_0(Fe^+{-}CH_2)$ value in refs 6c and 74, whereas the $^4B_2$ state was considered in ref 75.

(77) Carpenter, C. J.; van Koppen, P. A. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1995**, *117*, 10976.

(78) Another earlier estimate for the $D_0(Fe^+{-}C_2H_6)$ is 15.3 ± 1.4 kcal/mol. See: Schultz, R. H.; Armentrout, P. B. *J. Phys. Chem.* **1992**, *96*, 1662.

(79) (a) Reed, A. R.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (b) Reed, A. E.; Curtiss, L.A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (c) Weinhold, F.; Carpenter, J. E. In *The Structure of Small Molecules and Ions*; Naaman, R., Vager, Z., Eds.; Plenum Press: New York, 1988; p 227. (d) Reed, A. E.; Weinhold, F. *Isr. J. Chem.* **1991**, *31*, 277. For recent NPA applications, see, e.g.: (e) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434. (f) Glukhovtsev, M. N.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1992**, *198*, 547. (g) Mestres, J.; Duran, M.; Bertran, J. *Theor. Chim. Acta* **1994**, *88*, 325. (h) Nemukhin, A. V.; Grigorenko, B. L. *Chem. Phys. Lett.* **1995**, *233*, 627. (i) Glukhovtsev, M. N.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1995**, *117*, 2024.

(80) Holthausen, M. C.; Fiedler, A.; Schwarz, H.; Koch, W. *J. Phys. Chem.* **1996**, *100*, 6236.

(81) Rosi, M.; Bauschlicher, C. W.; Langhoff, S. R.; Partridge, H. *J. Phys. Chem.* **1990**, *94*, 8656.

(82) Ricca, A.; Bauschlicher, C. W.; Rosi, M. *J. Phys. Chem.* **1994**, *98*, 9498.

(83) (a) Schultz, R. H.; Crelin, K. C.; Armentrout, P. B. *J. Am. Chem. Soc.* **1991**, *113*. 8590. (b) Armentrout, P. B. *Acc. Chem. Res.* **1995**, *28*, 430.

(84) Hildenbrand, D. L. *J. Chem. Phys.* **1995**, *103*, 2634.

(85) Pouilly, B.; Schamps, J.; Lumley, D. J. W.; Barrow, R. F. *J. Phys. B* **1978**, *11*, 2281.