

## Surprisingly High Accuracy of ECP Methods for Predicting Fe–C Bond Dissociation Energies of FeCH<sub>3</sub><sup>+</sup>, FeCH<sub>2</sub><sup>+</sup> and FeCH<sup>+</sup>

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Theoretical studies using the extended effective core potential developed by Hay and Wadt (HW3) with a triply-split valence basis set at Fe and 6-31G(d) at C and H predict dissociation energies,  $E_{D,0}$ , for FeCH<sub>n</sub><sup>+</sup> ( $n = 1,2,3$ ) at the PMP4/HW3TZ, 6-31G(d) level which are in satisfactory agreement with experiment.

Accurate quantum mechanical calculations of the structures and energies of organometallic compounds usually need a very high level of theory, in particular for unsaturated systems.<sup>1</sup> Recently, McKee<sup>2</sup> showed that the trend for the Fe–C binding energies in FeCH<sub>n</sub><sup>+</sup> ( $n = 1,2,3$ ) is correctly reproduced when using effective core potentials (ECP) for Fe and a rather moderate (DZ) basis set for C and H at PMP3/ECPDZ. The absolute values for the Fe–C binding energies, however, were only *ca.* 60% of the experimental data.

We now report that the theoretically predicted Fe–C binding energies are significantly improved if a larger valence base is used for Fe. McKee<sup>2</sup> employed the ECP developed by Hay and Wadt<sup>3</sup> which has a valence base consisting only of the 3d<sup>6</sup>4s<sup>2</sup> electrons of Fe. The corresponding double-zeta valence basis set termed LANL1DZ is a standard basis set in Gaussian 90.<sup>4</sup> We used another ECP developed by Hay and Wadt<sup>5</sup> which has a valence base including the 3s<sup>2</sup>3p<sup>6</sup>3d<sup>6</sup>4s<sup>2</sup> electrons for Fe. The original basis set (55/5/5) for the s, p and d orbitals is split into (441/41/41)<sup>†</sup> and is termed by us HW3DZ. We also used the less contracted scheme (441/311/311) which is called HW3TZ. For C and H, we either used the Dunning–Huzinga<sup>6a</sup> double-zeta (DZ) or the 6-31G(d) basis set.<sup>6b</sup> All calculations have been carried out using the Convex version of Gaussian 90.<sup>4</sup>

The cations FeCH<sub>n</sub><sup>+</sup> ( $n = 1,2,3$ ) dissociate into Fe<sup>+</sup> and CH<sub>n</sub> in their electronic ground states. Table 1 shows the calculated two lowest-lying states of Fe<sup>+</sup>, the [core]4s<sup>1</sup>3d<sup>6</sup> (<sup>6</sup>D) ground state and the [core]3d<sup>7</sup> (<sup>4</sup>F) first excited state. At the correlated levels, the LANL1DZ ECP wrongly predicts that the <sup>4</sup>F state is the electronic ground state of Fe<sup>+</sup>. In contrast, calculations at the correlated levels using the HW3DZ and HW3TZ basis sets correctly predict that Fe<sup>+</sup> has a <sup>6</sup>D ground state. The calculated excitation energy <sup>6</sup>D→<sup>4</sup>F at PMP4 [4.8 kcal mol<sup>-1</sup> (1 cal = 4.184 J) (HW3DZ); 4.7 kcal mol<sup>-1</sup> (HW3TZ)] is in good agreement with the experimental value of 5.3 kcal mol<sup>-1</sup>.<sup>7</sup>

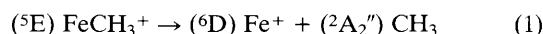
The geometries of the FeCH<sub>n</sub><sup>+</sup> cations and CH<sub>n</sub> fragments‡ in their electronic ground states§ have been optimized using Møller–Plesset perturbation theory<sup>8</sup> terminated at second order (MP2) with the different basis sets described above. The Fe–C bond energies are then calculated at the MP4 level using the MP2 optimized structures and the same basis sets.

† The s functions for the 3s and 4s orbitals have the same exponents (but different expansion coefficients). The s function with the smallest exponents was left uncontracted for the 4s orbital. Therefore, it was deleted from the set of 3s functions.

‡ The following results are calculated for the fragments CH<sub>n</sub> at MP2/DZ. (<sup>2</sup>A<sub>2</sub><sup>+</sup>) CH<sub>3</sub>:  $r(\text{CH})$  1.090 Å;  $\theta(\text{HCH})$  120.0°;  $E_{\text{tot}} = -39.6242$  hartrees. (<sup>3</sup>B<sub>1</sub>) CH<sub>2</sub>:  $r(\text{CH})$  1.089;  $\theta(\text{HCH})$  132.9°;  $E_{\text{tot}} = -38.9687$  hartrees. (<sup>2</sup>Π) CH:  $r(\text{CH})$  1.143;  $E_{\text{tot}} = -38.3038$ . The following results are calculated at MP2/6-31G(d). (<sup>2</sup>A<sub>2</sub><sup>+</sup>) CH<sub>3</sub>:  $r(\text{CH})$  1.078 Å;  $\theta(\text{HCH})$  120.0°;  $E_{\text{tot}} = -39.6730$  hartrees. (<sup>3</sup>B<sub>1</sub>) CH<sub>2</sub>:  $r(\text{CH})$  1.077;  $\theta(\text{HCH})$  131.6°;  $E_{\text{tot}} = -39.0074$  hartrees. (<sup>2</sup>Π) CH:  $r(\text{CH})$  1.120;  $E_{\text{tot}} = -38.3424$ .

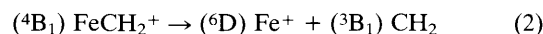
§ Extensive calculations by McKee<sup>2</sup> and by us show that the electronic states of FeCH<sub>n</sub><sup>+</sup> ( $n = 1,2,3$ ) discussed in our study are the ground states.

Spin-projection techniques are employed<sup>9</sup> to give more reliable energy values (PMP<sub>n</sub>) from the spin-unrestricted wave functions. Table 2 shows the results for (<sup>5</sup>E) FeCH<sub>3</sub><sup>+</sup> and for the calculated dissociation energies  $E_{\text{D}}$  of reaction (1).||



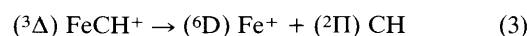
At PMP4/LANL1DZ, the Fe–C dissociation energy is 38.4 kcal mol<sup>-1</sup>. A significantly higher value of  $E_{\text{D}} = 44.7$  kcal mol<sup>-1</sup> is predicted at PMP4/HW3DZ (Table 2). Still higher bond energies are calculated at PMP4/HW3TZ ( $E_{\text{D}} = 47.4$  kcal mol<sup>-1</sup>) and, finally, by using a 6-31G(d) basis set for C and H at PMP4/HW3TZ, 6-31G(d),  $E_{\text{D}} = 49.9$  kcal mol<sup>-1</sup>. As expected, the highest calculated bond energy corresponds to the shortest Fe–C interatomic distance (1.953 Å) at MP2/HW3TZ, 6-31G(d).

Table 3 shows the calculated results for (<sup>4</sup>B<sub>1</sub>) FeCH<sub>2</sub><sup>+</sup> and for the dissociation reaction (2).|| At PMP4/LANL1DZ, the



dissociation energy for reaction (2) is calculated as 56.3 kcal mol<sup>-1</sup>. However, the <sup>6</sup>D state is not the ground state of Fe<sup>+</sup> at this level of theory (see Table 1). Dissociation of (<sup>4</sup>B<sub>1</sub>) FeCH<sub>2</sub><sup>+</sup> into the lowest lying electronic state of Fe<sup>+</sup> (<sup>4</sup>F) and (<sup>3</sup>B<sub>1</sub>) CH<sub>2</sub> at PMP4/LANL1DZ gives  $E_{\text{D}} = 47.7$  kcal mol<sup>-1</sup>. At PMP4/HW3DZ, the dissociation energy for reaction (2) is 54.7 kcal mol<sup>-1</sup>. Higher values are calculated at PMP4/HW3TZ ( $E_{\text{D}} = 57.3$  kcal mol<sup>-1</sup>) and at PMP4/HW3TZ, 6-31G(d) ( $E_{\text{D}} = 63.8$  kcal mol<sup>-1</sup>).

The calculated results for (<sup>3</sup>Δ) FeCH<sup>+</sup> and for the dissociation energies of reaction (3) are shown in Table 4.|| At first



sight, the theoretically predicted dissociation energies for reaction (3) using the extended HW3 ECP do not seem to show an improvement compared with LANL1DZ (Table 4). The calculated  $E_{\text{D}}$  value for reaction (3) at PMP4/HW3TZ (77.1 kcal mol<sup>-1</sup>) is practically the same as predicted at PMP4/LANL1DZ (77.4 kcal mol<sup>-1</sup>). However, as mentioned above, the <sup>6</sup>D state of Fe<sup>+</sup> is predicted to be an excited state at PMP4/LANL1DZ. The calculation of the Fe–C bond energy at this level of theory must refer to the <sup>4</sup>F state of Fe<sup>+</sup> and, therefore, has to be corrected by 8.6 kcal mol<sup>-1</sup> (Table 1). Thus, the Fe–C bond energy of (<sup>3</sup>Δ) FeCH<sup>+</sup> at PMP4/LANL1DZ is only 68.8 kcal mol<sup>-1</sup>. In contrast, the value obtained at PMP4/HW3TZ, 6-31G(d) is 80.4 kcal mol<sup>-1</sup> (Table 4).

In order to compare our calculated dissociation energies  $E_{\text{D}}$  with experimental values<sup>10</sup>  $E_{\text{D},0}$  at 300 K, zero-point vibrational energy (ZPE) differences and temperature corrections have to be estimated for reactions (1)–(3). The ZPE correction for reaction (1) has been taken from ref. 1(a) (2.6 kcal mol<sup>-1</sup>). We calculated the vibrational frequencies for FeCH<sub>2</sub><sup>+</sup> and FeCH<sup>+</sup> and the corresponding fragments at HF/HW3TZ,

|| The dissociation reactions (1)–(3) refer to the electronic ground states of the products and educts, irrespective of whether the reaction is symmetry-allowed or not. The calculated dissociation energies correspond to the Fe–C bond energies which have experimentally been measured using ion beam reactions of Fe<sup>+</sup> with various reactants and by thermochemical analysis of the products.<sup>10</sup>

**Table 1** Calculated and experimental energy difference (kcal mol<sup>-1</sup>) between the <sup>6</sup>D and <sup>4</sup>F states of Fe<sup>+</sup>; positive values indicate that <sup>6</sup>D is the electronic ground state of Fe<sup>+</sup>

	UHF	MP2	MP3	MP4	PUHF	PMP2	PMP3	PMP4	Expt. <sup>a</sup>
LANL1DZ	+23.6	-5.5	-1.6	-8.4	+23.2	-5.7	-1.8	-8.6	
HW3DZ	+32.8	+7.1	+12.6	+5.0	+32.5	+6.8	+12.4	+4.8	
HW3TZ	+34.8	+1.8	+12.5	+4.9	+34.4	+1.5	+12.4	+4.7	
									+5.3

<sup>a</sup> Ref. 7.**Table 2** Calculated results for (<sup>5</sup>E) FeCH<sub>3</sub><sup>+</sup> and dissociation energies  $E_D$  for the reaction (<sup>5</sup>E) FeCH<sub>3</sub><sup>+</sup> → (<sup>6</sup>D) Fe<sup>+</sup> + (<sup>2</sup>A<sub>2</sub><sup>g</sup>) CH<sub>3</sub><sup>a</sup>

	MP2			$E_D$			$E_{\text{tot}}$ (PMP4)
	$r(\text{Fe-C})$	$r(\text{C-H})$	$\theta(\text{Fe-C-H})$	PMP2	PMP3	PMP3	
LANL1DZ	2.039	1.103	109.2	36.8	36.0	38.4	-60.9907
HW3DZ	2.006	1.103	109.8	43.2	41.8	44.7	-162.1373
HW3DZ, 6-31G(d)	1.954	1.093	110.4	45.0	43.3	46.7	-162.1922
HW3TZ	2.001	1.103	109.2	46.3	44.0	47.4	-162.2135
HW3TZ, 6-31G(d)	1.953	1.094	109.8	48.9	46.0	49.9	-162.2691

<sup>a</sup> Distances in Å, angles in degrees,  $E_D$  in kcal mol<sup>-1</sup>,  $E_{\text{tot}}$  in hartrees.**Table 3** Calculated results for (<sup>4</sup>B<sub>1</sub>) FeCH<sub>2</sub><sup>+</sup> and dissociation energies  $E_D$  for the reaction (<sup>4</sup>B<sub>1</sub>) FeCH<sub>2</sub><sup>+</sup> → (<sup>6</sup>D) Fe<sup>+</sup> + (<sup>3</sup>B<sub>1</sub>) CH<sub>2</sub><sup>a</sup>

	MP2			$E_D$			$E_{\text{tot}}$ (PMP4)
	$r(\text{Fe-C})$	$r(\text{C-H})$	$\theta(\text{Fe-C-H})$	PMP2	PMP3	PMP4	
LANL1DZ	1.963	1.099	123.0	52.2	53.0	56.3	-60.3598
HW3DZ	1.939	1.099	122.4	51.3	51.3	54.7	-161.4938
HW3DZ, 6-31G(d)	1.889	1.088	123.0	56.5	56.3	60.3	-161.5451
HW3TZ	1.938	1.099	122.5	54.3	53.2	57.3	-161.5698
HW3TZ, 6-31G(d)	1.889	1.089	123.1	60.7	59.0	63.8	-161.6226

<sup>a</sup> Distances in Å, angles in degrees,  $E_D$  in kcal mol<sup>-1</sup>,  $E_{\text{tot}}$  in hartrees.**Table 4** Calculated results for (<sup>3</sup>Δ) FeCH<sup>+</sup> and dissociation energies  $E_D$  for the reaction (<sup>3</sup>Δ) FeCH<sup>+</sup> → (<sup>6</sup>D) Fe<sup>+</sup> + (<sup>2</sup>Π) CH<sup>a</sup>

	MP2			$E_D$			$E_{\text{tot}}$ (PMP4)
	$r(\text{Fe-C})$	$r(\text{C-H})$	$\theta(\text{Fe-C-H})$	PMP2	PMP3	PMP4	
LANL1DZ	1.896	1.095	180.0	75.2	73.7	77.4	-59.7305
HW3DZ	1.875	1.093	180.0	71.6	69.2	72.9	-160.8599
HW3DZ, 6-31G(d)	1.820	1.083	180.0	72.4	69.6	73.7	-160.9050
HW3TZ	1.866	1.094	180.0	76.1	72.2	77.1	-160.9386
HW3TZ, 6-31G(d)	1.813	1.083	180.0	79.7	75.1	80.4	-160.9876

<sup>a</sup> Distances in Å, angles in degrees,  $E_D$  in kcal mol<sup>-1</sup>,  $E_{\text{tot}}$  in hartrees.

6-31G(d) and scaled the ZPE values by 0.87.<sup>11</sup> This gave ZPE corrections of 2.2 kcal mol<sup>-1</sup> for reaction (2) and 2.3 kcal mol<sup>-1</sup> for reaction (3).<sup>¶</sup> Three degrees of translational freedom (1.5 *RT*) and 1 mol of Fe<sup>+</sup> (1 *RT*) are gained in reactions (1)–(3). This correction reduces the experimental  $E_{D,0}$  values at 300 K by 1.5 kcal mol<sup>-1</sup> to  $E_{D,0}$  values at 0 K.

Table 5 shows the calculated  $E_D$  and ZPE-corrected  $E_{D,0}$  values in comparison with other calculated results and experimental data. Our calculated dissociation energies are in much better agreement with experiment than the values calculated by McKee.<sup>2</sup> As discussed above, part of this improvement is caused by the larger valence base in the ECP calculations. Another difference in the accuracy is due to the

fact that McKee optimized the geometries of the molecules only at HF/LANL1DZ. It is noteworthy that the  $E_{D,0}$  value for FeCH<sub>3</sub><sup>+</sup> calculated at PMP4/HW3TZ, 6-31G(d) has about the same accuracy as predicted by Bauschlicher *et al.*<sup>10a</sup> using a large all-electron basis set for Fe and the modified coupled pair functional approach (MCPF).<sup>12</sup> For all three reactions (1)–(3), the calculated  $E_{D,0}$  values at PMP4/HW3TZ, 6-31G(d) account for more than 75% of the experimentally observed values. Since the experimental results are subject to an error of *ca.* 5%, the accuracy of the theoretical data may even be higher. It seems that the use of the extended ECP developed by Hay and Wadt<sup>5</sup> with a triply-split valence shell in conjunction with the MP4 procedure yields dissociation energies which are in satisfactory agreement with experiment. We will continue to investigate theoretically the accuracy of this level of theory for other small neutral and ionic organometallic molecules.

<sup>¶</sup> The calculated (unscaled) ZPE data are: 14.1 kcal mol<sup>-1</sup> (<sup>4</sup>B<sub>1</sub> FeCH<sub>2</sub><sup>+</sup>); 7.1 kcal mol<sup>-1</sup> (<sup>3</sup>Δ FeCH<sup>+</sup>); 11.6 kcal mol<sup>-1</sup> (<sup>3</sup>B<sub>1</sub> CH<sub>2</sub>); 4.4 kcal mol<sup>-1</sup> (<sup>2</sup>Π CH).

**Table 5** Calculated and experimentally obtained dissociation energies (kcal mol<sup>-1</sup>) for the Fe-C bond of (<sup>5</sup>E) FeCH<sub>3</sub><sup>+</sup>, (<sup>4</sup>B<sub>1</sub>) FeCH<sub>2</sub><sup>+</sup>, and (<sup>3</sup>Δ) FeCH<sup>+</sup>

	Calc.					Expt.
	$E_D^a$	$E_D^b$	$E_D^c$	$E_{D,0}^b$	$E_{D,0}^c$	$E_{D,0}^d$
FeCH <sub>3</sub> <sup>+</sup>	38.1	50.9	49.9	48.3	47.3	56.4 ± 2.4 <sup>e</sup>
FeCH <sub>2</sub> <sup>+</sup>	47.4		63.8		61.6	81.5 ± 4 <sup>f</sup>
FeCH <sup>+</sup>	68.2 <sup>h</sup>		80.4		78.1	101.5 ± 5 <sup>g</sup>

<sup>a</sup> McKee,<sup>2</sup> PMP3/LANL1DZ//HF/LANL1DZ. <sup>b</sup> Bauschlicher *et al.*,<sup>1a</sup> calculated results using all-electron basis sets and MCPF. <sup>c</sup> Our values at PMP4/HW3TZ, 6-31G(d)//MP2/HW3TZ, 6-31G(d). <sup>d</sup> Corrected by 1.5 kcal mol<sup>-1</sup> from  $E_{D,0}$  (300 K) to  $E_{D,0}$ . <sup>e</sup> Ref. 10a. <sup>f</sup> Ref. 10b. <sup>g</sup> Ref. 10c. <sup>h</sup>  $E_D$  relative to (<sup>4</sup>Σ<sup>-</sup>) CH.

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