High-Level ab Initio Predictions for the Ionization Energy, Bond Dissociation Energies, and Heats of Formations of Iron Carbide (FeC) and Its Cation (FeC^+)[†]

Kai-Chung Lau,*[,‡] Yih-Chung Chang,[§] Chow-Shing Lam,[§] and C. Y. Ng*[,§]

Department of Biology and Chemistry, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong, and Department of Chemistry, University of California, Davis, Davis, California 95616

Received: April 7, 2009; Revised Manuscript Received: August 20, 2009

The ionization energy (IE) of FeC and the 0 K bond dissociation energies (D_0) and the heats of formation at 0 K ($\Delta H°_{f0}$) and 298 K ($\Delta H°_{f298}$) for FeC and FeC^+ are predicted by the single-reference wave function based CCSDTQ(Full)/CBS approach, which involves the approximation to the complete basis set (CBS) limit at the coupled cluster level up to full quadruple excitations. The zero-point vibrational energy (ZPVE) correction, the core−valence electronic corrections (up to CCSDT level), spin−orbit couplings, and relativistic effects (up to CCSDTQ level) are included in the calculations. The present calculations provide the correct symmetry predictions for the ground states of FeC and FeC^+ to be $^3\Delta$ and $^2\Delta$, respectively. We have also examined the theoretical harmonic vibrational frequencies of FeC/FeC^+ at the ROHF-UCCSD(T) and UHF-UCCSD(T) levels. While the UHF-UCCSD(T) harmonic frequencies are in good agreement with the experimental measurements, the ROHF-UCCSD(T) yields significantly higher harmonic frequency predictions for FeC/FeC^+. The CCSDTQ(Full)/CBS IE(FeC) = 7.565 eV is found to compare favorably with the experimental IE value of 7.59318 ± 0.00006 eV, suggesting that the single-reference-based coupled cluster theory is capable of providing reliable IE prediction for FeC, despite its multireference character. The CCSDTQ(Full)/CBS $D_0(Fe^+{-}C)$ and $D_0(Fe{-}C)$ give the prediction of $D_0(Fe^+{-}C) - D_0(Fe{-}C) = 0.334$ eV, which is consistent with the experimental determination of 0.3094 ± 0.0001 eV. The D_0 calculations also support the experimental $D_0(Fe^+{-}C) = 4.1 \pm 0.3$ eV and $D_0(Fe{-}C) = 3.8 \pm 0.3$ eV determined by the previous ion photodissociation study. The present calculations also provide the $\Delta H°_{f0}(\Delta H°_{f298})$ predictions for FeC/FeC^+. The analysis of the correction terms in these calculations shows that the core−valence and valence−valence electronic correlations beyond CCSD(T) wave function and the relativistic effects make significant contributions to the calculated thermochemical properties of FeC/FeC^+. For the experimental D_0 and $\Delta H°_{f0}$ values of FeC/FeC^+, which are not known to high precision, we recommend the CCSDTQ(Full)/CBS predictions [$D_0(Fe{-}C) = 3.778$ eV, $D_0(Fe^+{-}C) = 4.112$ eV, $\Delta H°_{f0}(FeC) = 760.8$ kJ/mol and $\Delta H°_{f0}(FeC^+) = 1490.6$ kJ/mol] based on the ZPVE corrections using the experimental vibrational frequencies of FeC and FeC^+.

I. Introduction

Transition metal (M) containing molecules are known to play an important role in catalysis and astrophysics.[1,2] In order to discern the mechanisms and intermediates involved in catalytic processes and for modeling of the solar spectra of astrophysical interest, it is necessary to undertake spectroscopic and energetic characterizations of gaseous transition metal ligated species and their ions.[3−7] However, due to the difficulty in preparing transition metal containing molecules in the gas phase, the spectroscopic and energetic studies of these molecules remain relatively unexplored. Of the diatomic transition metal oxides, nitrides, carbides, and hydrides (MX, X = O, N, C, and H), only a few oxides have been subjected to high-resolution photoionization and photoelectron studies.[5−7] As a result, the energetic properties, such as ionization energies (IEs), 0 K bond dissociation energies (D_0's), and 0 K heats of formation ($\Delta H°_{f0}$) of most of these benchmarking MX and MX^+ species have not been determined to high precision.[1,2,5−8]

An equally difficult scenario exists for accurate theoretical predictions of IE, D_0, and $\Delta H°_{f0}$ values for transition metal containing species.[1] The difficulty arises from the existence of many unpaired d-shell electrons of the transition metal atom(s), which can give rise to a large number of low-lying electronic states of different multiplicities. Thus, the extent of electron correlation required and the correction effect due to spin−orbit couplings for the reliable theoretical treatments of transition metal compounds are significantly more sophisticated than molecules of the main-group elements. Nevertheless, due to the advance in ab initio quantum theoretical methodologies and the significant increase in computational capacity in recent years, reliable structural and energetic predictions for transition metal compounds have become feasible. Currently, the multireference configuration interaction (MRCI) methods are among the state-of-the-art ab initio quantum chemical procedures for structural and energetic calculations of transition metal containing species.[9,10]

Recently, Tzeli and Mavridis have reported detailed ab initio quantum calculations on the FeC/FeC^+ system at the C-MRCI+Q level of theory.[9,10] The latter calculations have taken into account the core−valence correlation effects, the Davidson correction, and scalar relativistic corrections and, thus, can be considered as the current most sophisticated calculations of the FeC/FeC^+ system. Stimulated by the spectroscopic constants for FeC/FeC^+

[†] Part of the "Vincenzo Aquilanti Festschrift".

* Corresponding authors, Kai-Chung Lau, kaichung@cityu.edu.hk, and C. Y. Ng, cyng@chem.ucdavis.edu.

[‡] City University of Hong Kong.

[§] University of California, Davis.

10.1021/jp903218h © 2009 American Chemical Society
Published on Web 09/23/2009

and IE(FeC), D_0(Fe−C), and D_0(Fe^+−C) values predicted by the C-MRCI+Q calculations, we have recently performed a high-resolution photoionization and photoelectron study of iron carbide (FeC) using the two-color laser photoionization efficiency (PIE) and pulsed field ionization-photoelectron (PFI-PE) schemes.[8] The completely rovibronically selected and resolved state-to-state PFI-PE transitions for FeC^+ observed near the photoionization threshold of FeC have allowed the unambiguous rotational assignment for the $FeC^+(X^2\Delta_{5/2}; v^+ = 0-2)$ vibrational bands. The finding of the $J^+ = 5/2$ level as the lowest rotational state confirms that the ground FeC^+ ion state is of $^2\Delta_{5/2}$ symmetry. We have also obtained the IE(FeC) = 7.59318 ± 0.00006 eV (61,243.1 ± 0.5 cm^{-1}) for the formation of FeC^+ ($X^2\Delta_{5/2}$, $v^+ = 0$; $J^+ = 5/2$) from FeC ($X^3\Delta_3$, $v'' = 0$; $J'' = 3$), and the vibrational constants $\omega_e{}^+ = 907.4$ cm^{-1} and $\omega_e{}^+\chi_e{}^+ = 3.24$ cm^{-1} for FeC^+ ($X^2\Delta_{5/2}$). Based on the conservation of energy, this experimental IE(FeC) value together with the known IE(Fe) = 7.9024 ± 0.0001 eV (63737.1 ± 0.8 cm^{-1}) gives the constraint for the difference of D_0(Fe^+−C) and D_0(Fe−C), i.e., IE(Fe) − IE(FeC) = D_0(Fe^+−C) − D_0(Fe−C) = 0.3094 eV.[8] Upon comparing this experimental values with the results of the C-MRCI+Q calculations of Tzeli and Mavridis,[9,10] we were surprised to find a large deviation of 0.5 eV for the IE(FeC) value and 0.2 eV for the D_0(Fe^+−C) − D_0(Fe−C) value. These large discrepancies have motivated us to undertake the present follow-up, large-scale ab initio quantum theoretical calculations for the thermochemical properties of FeC/FeC^+ for comparison with the highly precise experimental results.

By using the coupled cluster theory with single, double and perturbative triple excitations [CCSD(T)] together with the complete basis set (CBS) extrapolation technique, it has been shown that the ab initio CCSD(T)/CBS calculation is capable of providing accurate thermochemical predictions for molecules of main-group elements.[11−13] For example, we have benchmarked the theoretical IE predictions for a series of hydrocarbon radicals, including CH_2, CH_3, C_2H, C_2H_3, C_2H_5, C_3H_2, C_3H_3, C_3H_5, C_3H_7, C_4H_7, C_6H_5, and $C_6H_5CH_2$[14−17] and main-group compounds.[13] The theoretical predictions have taken into account the zero-point vibrational energy (ZPVE), core−valence (CV), scalar-relativistic (SR), and higher-order corrections (HOC) beyond the CCSD(T) wave function. On the basis of the comparison between the CCSD(T)/CBS IE predictions and the experimental IE values of selected hydrocarbon radicals, we have concluded that the CCSD(T)/CBS method could give accurate IE predictions to within ±10 meV for CH_2, CH_3, C_2H, C_2H_3, C_2H_5, C_3H_3, C_3H_5, and C_3H_7,[14−16] and ±20 meV for C_4H_7 radicals.[17] Furthermore, the comparison between the highly precise experimental IE($C_6H_5CH_2$) value and the theoretical CCSD(T)/CBS prediction has allowed us to assign the upper error limit of about ±35 meV for the CCSD(T)/CBS approach to the IE predictions of C7 hydrocarbon radicals.[15]

Very recently, Balabanov and Peterson have developed correlation consistent basis sets for the 3d transition elements.[18] These correlation consistent basis sets, which are similar to those for main-group elements,[19] exhibit systematic convergence toward complete basis set limit by extrapolation when two or three successive basis sets are used. The performance of this series of correlation consistent basis sets is found to be reliable at the Hartree−Fock, density functional theory, and couple cluster methods.[20−22] Encouraged by the good agreement observed between the ab initio predictions and experimental IE values for the hydrocarbon radicals, we now extend the CCSD(T)/CBS IE calculations for FeC, whose IE value has been measured[8] with an uncertainty of 0.5 cm^{-1}. In the present calculations, the correlation consistent basis set series for the 3d transition elements of Balabanov and Peterson is used.[18] Due to the simplicity of the FeC/FeC^+ molecules, we have further included the core−valence electronic correlation at the CCSDT level, the scalar-relativistic effect at the CCSDTQ level, and higher-order corrections at the couple cluster level with up to full triple and quadruple excitations. Overall, the level of theory at which theoretical predictions are presented in this work is effectively at the CCSDTQ(Full)/CBS level. "Full" denotes the electronic correlations are included for the outer-core 3s3p and valence 4s3d electrons on Fe and all the 1s2s2p electrons on C. The comparison between the highly precise experimental IE(FeC) value and the CCSDTQ(Full)/CBS theoretical predictions presented here would serve to benchmark the current CCSDTQ(Full)/CBS approach for reliable IE predictions of transition metal containing compounds. More importantly, the performance of single-reference based CCSDTQ(Full)/CBS approach for the thermochemistry predictions of multireferenced molecule is examined. Besides reporting the IE value of FeC, we also present the theoretical predictions for the D_0(Fe−C), D_0(Fe^+−C), ΔH°_f(FeC) and ΔH°_f(FeC^+) and a comparison of these results with available experimental data.

II. Theoretical Calculations

There have been three coupled cluster approaches for treating open-shell molecules. We have chosen to use the partially unrestricted implementation, conventionally labeled as ROHF-UCCSD(T) for the energetic, vibrational frequencies and correlation calculations of FeC/FeC^+. This method is based on restricted open-shell Hartree−Fock (ROHF) orbitals and relaxes the spin restriction throughout the coupled cluster calculation.[23,24] The other two approaches are the completely unrestricted method based on unrestricted Hartree−Fock (UHF) orbitals and the partially restricted approach based on ROHF orbitals, which are labeled as UHF-UCCSD(T) and ROHF-RCCSD(T),[25−27] respectively. As shown below, since the ROHF-UCCSD(T) method does not yield satisfactory results on the harmonic vibrational frequencies of FeC/FeC^+, the UHF-UCCSD(T) method has also been used to predict the harmonic vibrational frequencies calculations. All the coupled cluster calculations described below are based on the ROHF orbitals level unless specified.

A. Extrapolated Valence Correlation Energy and Zero-Point Vibrational Energy Correction. Our calculations first involve the approximation to the CBS limit at the CCSD(T) level of theory. The structures of the ground states FeC ($^3\Delta$) and FeC^+ ($^2\Delta$) have been optimized at the CCSD(T) level with successively larger basis sets, proceeding from aug-cc-pwCVTZ, to aug-cc-pwCVQZ and then to aug-cc-pwCV5Z. The aug-cc-pwCV*X*Z (X = 3, 4 and 5) basis sets are the Dunning's correlation consistent polarization weighted core−valence correlation first proposed[28] in 2002 and were extended to 3d transition elements recently.[18] Besides the valence 2s2p electrons on carbon and 4s3d electrons on Fe, the geometrical optimizations also correlate the core 1s electrons on carbon and outer-core 3s3p electrons on Fe. The 1s2s2p electrons on Fe are kept frozen and uncorrelated. The CBS energies ($E_{\text{extrapolated CBS}}$) are estimated by two different extrapolation schemes:

(i) A three-point extrapolation scheme[29] using the mixed exponent/Gaussian function of the form

$$E(X) = E_{\text{extrapolated CBS}} + B\exp[-(X-1)] + C\exp[-(X-1)^2] \quad (1)$$

where $X = 3$, 4, and 5 for aug-cc-pwCVTZ, aug-cc-pwCVQZ, and aug-cc-pwCV5Z, respectively. Here, we denote the CBS energies extrapolated directly from the CCSD(T) energy using eq 1 with successive aug-cc-pwCV[T-5]Z basis sets as CBS_{wCTQ5}.

(ii) A two-point extrapolation scheme[30,31] using the simple power function involving the reciprocal of X

$$E(X) = E_{\text{extrapolated CBS}} + \frac{B}{X^3} \tag{2}$$

where $X = 4$ and 5 for aug-cc-pwCVQZ and aug-cc-pwCV5Z, respectively. We denote the extrapolated CBS energies directly from the CCSD(T) valence energy using eq 2 with the aug-cc-pwCV[Q,5]Z basis sets as CBS_{wCQ5}. Unless specified, the harmonic vibrational frequencies at the CCSD(T)/aug-cc-pV5Z level are used for the zero-point vibrational energy corrections (ΔE_{ZPVE}).

B. Higher-Order Correlation. The higher-order energy contributions (ΔE_{HOC}) beyond the CCSD(T) theory are critical for the accurate thermochemical predictions. In our previous studies, the HOC makes a significant contribution (9 meV) to the IE prediction of the ethynyl radical.[14] The HOC correction incorporates higher-order triple and quadruple excitations, where the full triple excitation effect is estimated by the difference between CCSDT and CCSD(T) energies and the iterative quadruple excitations are estimated as the difference of CCSDTQ − CCSDT energies. The HOC for FeC/FeC^+ is represented by the sum

$$E_{HOC} = E_{CCSDT/aug\text{-}cc\text{-}pVQZ} - E_{CCSD(T)/aug\text{-}cc\text{-}pVQZ} + E_{CCSDTQ/cc\text{-}pVTZ} - E_{CCSDT/cc\text{-}pVTZ} \tag{3}$$

C. Scalar Relativistic Effect. The scalar relativistic (SR) energy is computed using the spin-free, one-electron Douglas−Kroll−Hess (DKH) Hamiltonian.[32,33] The calculations are done with the DKH-contracted aug-cc-pV5Z-DK basis sets[18,34] at the CCSD(T) level. The SR energetic contributions are taken as the differences between electronic energies at the CCSD(T)/aug-cc-pV5Z level without using the DKH Hamiltonian and at the CCSD(T)/aug-cc-pV5Z-DK level with the DKH Hamiltonian. The relativistic effect due to the full triple and quadruple excitations has also been included in a similar manner as described in eq 3, except that the aug-cc-pVQZ-DK and cc-pVTZ-DK basis sets are used for the corresponding CCSDT and CCSDTQ calculations.

D. Core−Valence Electronic Correction Beyond CCSD(T). The electronic correlation contributions between the core and valence electrons and those within core electrons have already been included in the single-point energy and geometrical optimization calculations at the CCSD(T) level. Additional core−valence electronic correlations (E_{CV}) from the full triple excitations are obtained as the energy difference between CCSD(T) and CCSDT levels with the cc-pwCVTZ basis set.[18,28] The core 1s electrons on carbon and outer-core 3s3p electrons on Fe are correlated in the calculations.

E. Spin−Orbit (SO) Coupling. The molecular spin−orbit coupling (E_{SO}) of the FeC and FeC^+ are computed by first-order perturbation theory. The calculations used an uncontracted aug-cc-pVTZ basis set including the s, p, d, and f functions on Fe and the s, p, d functions on C. Spin−orbit matrix elements were computed among the components of the FeC and FeC^+ states using the internally contracted multireference configuration interaction wave function.[35] The 2s2p electrons on C and the 4s3d electrons on Fe were included in the active space. The atomic SO coupling corrections of Fe and Fe^+ are done in similar manner. The atomic SO correction (0.37 kJ/mol) for carbon is directly taken from the experimental excitation energies tabulated by Moore.[36]

In the present work, all the CCSD(T) single-point energy calculations, vibrational frequency calculations, and correlation contributions were performed using the MOLPRO 2008.1[37] and the CCSDT and CCSDTQ were done with the string-based many-body MRCC program[38] interfaced with MOLRPO. The $\Delta H°_{f0}$ and $\Delta H°_{f298}$ values for the FeC and FeC^+ were calculated using the atomization scheme[39] and the following experimental values:[40] $\Delta H°_{f0}(C) = 711.2$ and $\Delta H°_{f0}(Fe) = 414$, $\Delta H°_{f298}(C) = 716.7$, and $\Delta H°_{f298}(Fe) = 415.5$ kJ/mol.

III. Results and Discussion

At the single-reference CCSD(T) level, the ground electronic state of FeC is predicted to have the $^3\Delta$ symmetry with the electronic configuration of ... $7\sigma^2 8\sigma^2 3\pi^4 1\delta^3 9\sigma^1$. This prediction agrees with the previous experimental determinations and multireference based ab initio calculations. The valence electrons of FeC are contributed by the $4s^2 3d^6$ electrons of Fe and the $2s^2 2p^2$ electrons of C. Due to the energy mismatch or offset of atomic orbitals of Fe and C, the 7σ orbital is overwhelmingly dominated by the C(2s) character. Assuming that the FeC molecule lies along the z-axis, the 8σ orbital is formed by the overlap of the $Fe(3d_{z^2})$ and $C(2p_z)$ orbitals and is shown to have the major contribution from the $Fe(3d_{z^2})$ orbital. The two degenerate π bonding orbitals, $3\pi_x$ and $3\pi_y$, are formed by the overlaps of $Fe(3d_{xz})$ and $C(2p_x)$ and $Fe(3d_{yz})$ and $C(2p_y)$, respectively. The 1δ orbitals are nonbonding in nature, consisting of the $Fe(3d_{xy})$ and $Fe(3d_{x^2-y^2})$ orbitals. Taking into account the electrostatic interaction, these two nonbonding orbitals are expected to have slightly different energies. The 9σ orbital is shown to have the dominant Fe(4s) character and, thus, is mostly nonbonding in nature. The triplet nature of the ground state electronic configuration of FeC results from the close energy spacing of the 1δ and 9σ orbitals. On the basis of the Mulliken population analysis, the $FeC(X^3\Delta)$ ground state can be viewed to have a Fe≡C triple bond, consisting of two π ($3\pi^4$) and one σ ($8\sigma^2$) bonds.[9] According to the predicted ground state electronic configuration for FeC, the first ionization would involve the removal of the unpaired electron in the 9σ orbital, resulting in the formation of the $^2\Delta$ ground electronic state for FeC^+. The formation of the $FeC^+(X^2\Delta_{5/2})$ ground state has been confirmed in our recent PFI-PE study.[8] Thus, the triple bond in FeC is expected to be nearly unaffected by the process of ionization. The correct prediction of the $FeC(X^3\Delta)$ and $FeC^+(X^2\Delta_{5/2})$ ground states represents a triumph for the ab initio quantum calculations.[8−10]

A. Structures and Harmonic Vibrational Frequencies of FeC and FeC^+. The bond lengths r_e (r_e^+) and harmonic vibrational frequencies ω_e (ω_e^+) of $FeC(X^3\Delta)$ [$FeC^+(X^2\Delta)$] predicted at the CCSD(T)/aug-cc-pVXZ and CCSD(T)/aug-cc-pwCVXZ levels are summarized in Table 1. The calculations at the CCSD(T)/aug-cc-pwCVXZ level have included the core−valence and valence−valence electronic correlations for the 3s3p4s4p electrons on Fe and 1s2s2p electrons on C. Included in Table 1 are the theoretical r_e (r_e^+) and ω_e (ω_e^+) values for the neutral and cation obtained in the C-MRCI+Q calcuations,[9,10] and the highly precise experimental results for the neutral[3,41] and the cation.[8]

As shown in Table 1, the CCSD(T) predicted r_e values for FeC are in the range from 1.577 to 1.571 Å with successively

TABLE 1: The Bond Length r_e (r_e^+) in Å and Harmonic Vibrational Frequency ω_e (ω_e^+) in cm^{-1} for FeC($X^3\Delta$) [FeC$^+$ ($X^2\Delta$)] Predicted at the ROHF-UCCSD(T)/aug-cc-pVXZ and ROHF-UCCSD(T)/aug-cc-pwCV*XZ* Levels, Where X = T, Q, and 5

	FeC ($^3\Delta$)		FeC$^+$ ($^2\Delta$)	
	r_e	ω_e	r_e^+	ω_e^+
aug-cc-pVTZ	1.577	1114	1.560	1180
	1.577[a]	845[a]	1.558[a]	901[a]
aug-cc-pVQZ	1.573	1155	1.555	1230
aug-cc-pV5Z	1.571	1175	1.554	1251
aug-cc-pwCVTZ	1.565	1290	1.550	1368
aug-cc-pwCVQZ	1.562	1345	1.547	1419
aug-cc-pwCV5Z	1.561	1373	1.546	1440
C-MRCI+Q[b]	1.598	877	1.557	928
experimental	1.596[c]	862.9±6.2[d]	1.559[e]	927.14[e]

[a] Calculated at the UHF-UCCSD(T) level. [b] Taken from values at the C-MRCI+Q level in refs 9 and. 10. [c] Reference 3. [d] Reference 41. [e] Reference 8.

increasing basis set size from aug-cc-pVTZ to aug-cc-pV5Z. Included with the core−valence correlation effect, the bond lengths at all three basis sets are decreased by about 0.01 Å. All the predicted CCSD(T) bond lengths for FeC are shorter than the C-MRCI+Q prediction of 1.598 Å obtained by Tzeli and Marvidis.[9] The latter value is almost in exact agreement with the experimental value of 1.596 Å.[3] Similar shortening in the r_e value was also found in the previous MRCI study when the 3s3p electrons are correlated.

The CCSD(T) ω_e values of FeC range from 1114 to 1175 cm^{-1} over the three aug-cc-pVXZ basis sets. The predictions are significantly higher than the C-MRCI value[9] of 877 cm^{-1} and the experimental value of 862.9 ± 6.2 cm^{-1}.[41] Inclusion of the core−valence correlation effect does not improve the predictions but rather yields even larger vibrational frequencies. The predicted vibrational frequencies at the aug-cc-pV5Z and aug-cc-pwCV5Z significantly deviate from the experimental value by more than 300 and 500 cm^{-1}, respectively. The large discrepancies in the harmonic vibrational frequencies between the CCSD(T) predictions and experimental value suggest that the ROHF based CCSD(T) theory may be inadequate in describing the curvature of the potential energy surface around the equilibrium structure of ground state FeC.

To shed light on the vibrational frequencies predictions for FeC/FeC$^+$ with the CCSD(T) methods, we have performed additional harmonic vibrational frequencies calculations for the ground state of FeC/FeC$^+$ using the ROHF-based RCCSD(T) and completely spin-relaxed UCCSD(T) implementations. The calculated ω_e/ω_e^+ at the ROHF-UCCSD(T), ROHF-RCCSD(T), and UHF-UCCSD(T) levels with the aug-cc-pVTZ basis set are 1114/1180, 1193/1186, and 845/901 cm^{-1}, respectively. The optimized r_e/r_e^+ at the ROHF-UCCSD(T), ROHF-RCCSD(T), and UHF-UCCSD(T) levels using the aug-cc-pVTZ basis set are 1.577/1.560, 1.575/1.558, and 1.577/1.558 Å, respectively. The theoretical ω_e/ω_e^+ and r_e/r_e^+ values calculated at the UHF-UCCSD(T)/aug-cc-pVTZ level are also included in Table 1. While the optimized bond distances r_e/r_e^+ are very similar among the three CCSD(T) methods, significant large discrepancies are found among the calculated vibrational frequencies. The harmonic vibrational frequencies obtained at the UHF-UCCSD(T)/aug-cc-pVTZ level are in line with the experimental ω_e/ω_e^+ values. We have examined the ground state potential energy surface of FeC in the vicinity of the potential minimum at the distances of $r_e \pm 0.005$, $r_e \pm 0.010$, and $r_e \pm 0.015$ Å using the ROHF-UCCSD(T) and UHF-UCCSD(T) methods. The potential energy surface near the potential well of FeC at the ROHF-UCCSD(T)/aug-cc-pVTZ level is found to be steeper than that at the UHF-UCCSD(T)/aug-cc-pVTZ level. As the force constant (second derivative of energy with respect to bond distance) is directly proportional to the curvature of the potential energy surface near the potential well, the vibrational frequency (proportional to the square root of force constant) at the ROHF-UCCSD(T)/aug-cc-pVTZ level is significantly larger than that at the UHF-UCCSD(T)/aug-cc-pVTZ level for FeC. The same observation is found in the comparison of the potential energy surfaces near the FeC$^+$ minimum obtained at the ROHF-UCCSD(T) and UHF-UCCSD(T) levels. As the density functional theory has been extensively used for structural and energetic predictions of transition-metal compounds,[42] we have also performed relevant calculations for FeC/FeC$^+$ at the B3YLP/aug-cc-pVTZ level, yielding the r_e/r_e^+ and ω_e/ω_e^+ values of 1.610/1.557 Å and 593/613 cm^{-1}, respectively. The latter vibrational frequency predictions are much smaller than the experimental values, indicating that the DFT calculation at the B3YLP/aug-cc-pVTZ level is not an accurate theoretical method for the spectroscopic calculations of FeC/FeC$^+$.

Our recent rovibronically selected and resolved state-to-state PFI-PE study gives $r_e^+ = 1.559$ Å and $\omega_e^+ = 927.14 \pm 0.04$ cm^{-1} for the ground state of FeC$^+$.[8] The slight contraction of 0.037 Å observed for the bond distance from $r_e = 1.596$ Å to $r_e^+ = 1.559$ Å upon ionization is consistent with the bonding analysis that the 9σ orbital is mostly nonbonding in nature. Similar shortening in bond length is confirmed by both the C-MRCI+Q and CCSD(T) calculations.[8−10] Comparing the theoretical predictions with these experimental r_e^+ and ω_e^+ values, we find that the C-MRCI+Q calculation of Tzeli and Marvidis[10] again provides excellent predictions for $r_e^+ = 1.557$ Å and $\omega_e^+ = 928$ cm^{-1}. The present CCSD(T) predictions on the bond length of FeC$^+$ are found to be insensitive to the basis set effect with the r_e^+ values in the range from 1.560 Å (aug-cc-pVTZ) to 1.554 Å (aug-cc-pV5Z). These values are in good accord with the experimental determination. Similar to the calculations of the neutral FeC, the bond length for the cation is found to decrease by 0.01 Å when the core−valence correlation is taken into account.

Likewise to the comparison of the experimental and theoretical vibrational frequencies for the neutral, the CCSD(T) harmonic vibrational frequencies for FeC$^+$ are considerably higher than the experimental frequency[8] by 253 (aug-cc-pVTZ) to 324 cm^{-1} (aug-cc-pV5Z). When the core−valence correlation effect is included, it is disappointing to see the deviations of CCSD(T) predictions from the experimental value become even larger. The large discrepancy observed between the experimental and CCSD(T) harmonic frequencies for FeC$^+$ is again indicative of the potential deficiency of the ROHF-UCCSD(T) approach for vibrational frequency calculations of transition metal containing species.

B. Ionization Energy of FeC. FeC and FeC$^+$ are known to have many low-lying excited states, giving rise to their multireference characters. Thus, it is of great interest to examine whether the single-reference coupled cluster theory can provide reliable energetic predictions for FeC/FeC$^+$ and other transition metal containing species.[9,10] The individual energy corrections ($\Delta E_{\text{extrapolated CBS}}$, ΔE_{CV}, ΔE_{ZPVE}, ΔE_{SO}, ΔE_{SR}, and ΔE_{HOC}) for the IE(FeC), IE(Fe), D_0(FeC), and D_0(FeC$^+$) predictions are listed in Table 2. The CCSDTQ(Full)/CBS IE(Fe) = 7.900 eV is found to be in excellent agreement with the experiment IE(Fe) = 7.9024 ± 0.0001 eV.[44] For the IE(Fe) prediction, the major corrections are $\Delta E_{\text{SR}} = 0.094$ eV and $\Delta E_{\text{HOC}} = 0.011$ eV. The average of the $\Delta E_{\text{extrapolated CBS}}$ contributions to the IE(FeC) values

TABLE 2: Individual Energy Contributions to the CCSDTQ(Full)/CBS Predictions for the IE(FeC), IE(Fe), D_0(Fe−C), and D_0(Fe$^+$−C) Predictions[a]

		IE(FeC)	IE(Fe)	D_0(Fe−C)	D_0(Fe$^+$−C)
$\Delta E_{\text{extrapolated CBS}}$[b]	wCTQ5	7.425	7.799	3.770	4.144
	wCQ5	7.426	7.802	3.799	4.176
	average	7.426	7.801	3.785	4.160
ΔE_{CV}[c]	(T) → T	0.008	−0.005	−0.006	−0.018
ΔE_{ZPVE}[d]		0.005		−0.073	−0.078
		0.004[e]		−0.053[e]	−0.057[e]
ΔE_{SO}[f]		−0.039	−0.001	−0.049	−0.012
ΔE_{SR}[g]	CCSD(T)	0.147	0.093	−0.088	−0.142
	(T) → T	0.002	0.000	0.001	−0.001
	T → Q	−0.005	0.001	0.000	0.005
	subtotal	0.144	0.094	−0.087	−0.138
ΔE_{HOC}[h]	(T) → T	−0.013	0.008	−0.162	−0.142
	T → Q	0.034	0.003	0.350	0.320
	subtotal	0.021	0.011	0.188	0.178
CCSDTQ(Full)/CBS IE or D$_0$[I]		7.565	7.900	3.758	4.092
		7.564[e]		3.778[e]	4.112[e]
experimental		7.59318 ± 0.00006[j]	7.9024 ± 0.0001[l]	3.8 ± 0.3[m]	4.1 ± 0.3[o]
		7.74 ± 0.09[k]		3.4 ± 0.2[n]	3.7 ± 0.2[p]

[a] All quantities and energy differences are in electronvolts. [b] Extrapolated from the core and valence correlation energies using eqs 1 and 2 with the aug-cc-pwCV[T-5]Z and aug-cc-pwCV[Q,5]Z basis sets, respectively. [c] Core−valence electronic correlation obtained as the energy difference between CCSD(T) and CCSDT levels using the cc-pwCVTZ basis set. [d] Based on the harmonic vibrational frequencies at the CCSD(T)/aug-cc-pV5Z level. [e] Values obtained using the experimental vibrational frequencies of FeC/FeC$^+$ for ZPVE corrections. [f] Spin−orbit coupling obtained at the MRCI level with the uncontracted cc-pVTZ basis set. [g] Scalar relativistic effect calculated at the CCSD(T)/aug-cc-pV5Z-DK, CCSDT/aug-cc-pVQZ-DK and CCSDTQ/cc-pVTZ-DK levels. [h] Higher-order effect calculated at the CCSDT/aug-cc-pVQZ and CCSDTQ/cc-pVTZ levels. [I] IE or $D_0 = \Delta E_{\text{extrapolated CBS}} + \Delta E_{\text{CV}} + \Delta E_{\text{ZPVE}} + \Delta E_{\text{SO}} + \Delta E_{\text{SR}} + \Delta E_{\text{HOC}}$. [j] Reference 8. [k] Reference 4. [l] Reference 44. [m] The value of D_0(Fe−C) is deduced based on D_0(Fe$^+$−C) = 4.1 ± 0.3, IE(FeC) = 7.59318 ± 0.00006 eV, and IE(Fe) = 7.9024 ± 0.0001 eV. [n] The value of D_0(Fe−C) is deduced based on D_0(Fe$^+$−C) = 3.7 ± 0.2, IE(FeC) = 7.59318 ± 0.00006 eV, and IE(Fe) = 7.9024 ± 0.0001 eV. [o] Reference 43. [p] Reference 47.

based on the two- and three-point extrapolation methods is 7.426 eV. The ΔE_{ZPVE} correction for IE(FeC) obtained using the harmonic vibrational frequencies at the CCSD(T)/aug-cc-pV5Z level, is 0.005 eV. Although our predicted harmonic vibrational frequencies for FeC/FeC$^+$ deviate from the experimental values over 300 cm^{-1}, the latter ΔE_{ZPVE} contribution for IE(FeC) is nearly identical to the ΔE_{ZPVE} correction (0.004 eV) calculated with the experimental harmonic frequencies because ΔE_{ZPVE} depends only on difference ($\omega_e^+ - \omega_e$) of the vibration frequencies. Thus, the ΔE_{ZPVE} correction obtained using the inaccurate CCSD(T)/aug-cc-pV5Z vibrational frequencies of FeC/FeC+ is expected to have only negligible effect on theoretical IE(FeC) prediction. This also explains the observation that the ΔE_{ZPVE} contribution is essentially invariant to the basis set effect. The core−valence electronic contribution due to the full triple excitation beyond the CCSD(T) wave function calculated with cc-pwCVTZ basis set is 0.008 eV. As expected, the relativistic effect plays an important role for the thermochemistry predictions of transition-metal compounds, its contribution to the IE(FeC) at the CCSD(T)/aug-cc-pV5Z level is 0.147 eV. Together with the relativistic effects from the full triple and quadruple excitations, we obtain an overall ΔE_{SR} contribution of 0.144 eV to the IE(FeC) value. The higher-order correction, consisting of full triplet and quadruple excitations beyond CCSD(T) theory, make a significant contribution of 0.021 eV to the IE(FeC) value. The CCSDT and CCSDTQ calculations are performed with the aug-cc-pVQZ and cc-pVTZ basis sets, respectively. Putting all the correlation contributions together, we have arrived a value of 7.565 eV for IE(FeC) at the CCSDTQ(Full)/CBS level included with the core−valence electronic correlations (up to CCSDT level), relativistic effect (up to CCSDTQ level), higher-order correction (up to CCSDTQ level), harmonic ZPVE correction, and spin−orbit couplings. It is encouraging to find that our predicted IE value comes to less than 30 meV below the highly precise experimental value of 7.59318 ± 0.00006 eV.[8] The excellent agreement between our prediction and measured values for IE(FeC) suggests that the single-reference based coupled cluster theory is capable of predicting the IE(FeC) value within the chemical accuracy (±4 kJ/mol). In this IE(FeC) prediction, we have found that the contribution from the relativistic effect is significant (over 0.14 eV). Inclusions of the core−valence and valence−valence electronic correlations beyond CCSD(T) wave function are critical (together they make a contribution of +29 meV) for bringing our IE(FeC) prediction closer to the experimental value. Compared with the experimental IE(FeC) value, our current IE(FeC) prediction at the CCSDTQ(Full)/CBS level is significantly more accurate than the previous prediction (7.10 eV) of Tzeli and Marvidis[9] calculated with the C-MRCI+Q method (using the atomic natural orbital basis for Fe and cc-pVQZ basis for C), which included the core−valence correlation effects, Davidson correction, and scalar relativistic effect.

We have recently completed a similar IE prediction for nickel carbide (NiC)[45] and found that the CCSDTQ(Full)/CBS IE(NiC) is also in excellent agreement with the experimental determination[46] based on rotationally resolved photoionization and photoelectron measurements. This observation indicates that the agreement between the theoretical CCSDTQ(Full)/CBS IE(FeC) prediction and the experimental IE(FeC) measurement as presented here is not accidental.

C. 0 K Dissociation Energies of Fe−C and Fe$^+$−C. On the basis of the cation thermochemical cycle, we can show that the IE(FeC), IE(Fe), D_0(Fe−C), and D_0(Fe$^+$−C) are related by the following equation

$$D_0(\text{Fe}{-}\text{C}) + \text{IE(Fe)} = \text{IE(FeC)} + D_0(\text{Fe}^+{-}\text{C}) \qquad (4)$$

While the experimental IE(FeC) = 7.59318 ± 0.00006 eV and IE(Fe) = 7.9024 ± 0.0001 eV[44] are accurately known, the experimental D_0(Fe−C) and D_0(Fe^+−C) values have not yet been determined with high precision. Using the IE(FeC) and IE(Fe) together with the D_0(Fe^+−C) value of 94 ± 7 kcal/mol (or 4.1 ± 0.3 eV) determined from the early photodissociation measurement[43] of Hettich and Freiser, we arrive at an experimental value of 3.8 ± 0.3 eV for D_0(Fe−C). The uncertainty of this D_0(Fe−C) value is large and depends heavily on that of the D_0(Fe^+−C) value. Our predicted values for D_0(Fe^+−C) = 4.092 eV and D_0(Fe−C) = 3.758 eV calculated at the CCSDTQ(Full)/CBS level are in excellent accord with the experimental D_0(Fe^+−C) of 4.1 ± 0.3 eV and the deduced D_0(Fe−C) value of 3.8 ± 0.3 eV, respectively. Referring to the individual energetic contributions to the CCSDTQ(Full)/CBS predictions for D_0(Fe−C) and D_0(Fe^+−C) listed in Table 2, we found that the most significant energetic corrections in the D_0(Fe−C) and D_0(Fe^+−C) predictions are from the relativistic effect and the higher-order corrections beyond the CCSD(T) wave function. The respective ΔE_{SR} contributions to the D_0(Fe−C) and D_0(Fe^+−C) predictions are −0.087 and −0.138 eV, whereas the ΔE_{HOC} contributions are 0.188 and 0.178 eV. The ΔE_{HOC} contributions from higher-order coupled cluster excitations are large (in absolute value) but opposite compared with the ΔE_{SR} contributions, and if either the relativistic or the higher-order correction is ignored in the D_0 predictions, the agreement between theoretical predictions and experimental measurements would become worse. We note that there is another experimental D_0(Fe^+−C) value of 84.2 ± 4.1 kcal/mol (or 3.7 ± 0.2 eV) deduced recently by Angeli et al.[47] based on the measured appearance threshold for the dissociation reaction of $Fe(CO)_5 \rightarrow FeC^+ + O + 4CO + e^-$. Using this experimental D_0(Fe^+−C) of 3.7 ± 0.2 eV, together with the known IE(FeC) and IE(Fe) values, a lower experimental value for D_0(Fe−C) of 3.4 ± 0.2 eV is obtained. Considering the fact that our theoretical prediction is much closer to the value D_0(Fe^+−C) = 4.1 ± 0.3 eV by Hettich and Freiser,[43] we believe that the D_0(Fe^+−C) value of 3.7 ± 0.2 eV deduced from the appearance threshold measurement by Angeli et al. may be too low. The formation of FeC^+ from dissociative photoionization of $Fe(CO)_5$ is expected to involve sequential dissociation processes, and thus, the appearance energy of FeC^+ reported by Angeli et al.[47] may suffer from a larger uncertainty than their reported error limit.[43] In the current CCSDTQ(Full)/CBS calculations of D_0(Fe−C) and D_0(Fe^+−C), we have obtained the ZPVE correction based on the harmonic vibrational frequencies at the CCSD(T)/aug-cc-pV5Z level. As we mentioned before, the CCSD(T)/aug-cc-pV5Z harmonic vibrational frequencies deviate significantly from the experimental harmonic vibrational frequencies. If the experimental harmonic vibrational frequencies of the FeC and FeC^+ are used for ΔE_{ZPVE} correction in the D_0 predictions, the present values for the D_0(Fe−C) and D_0(Fe^+−C) should be increased by about 20 meV, yielding D_0(Fe−C) = 3.778 eV and D_0(Fe^+−C) = 4.112 eV. Although the difference of 20 meV is small compared to the uncertainties of 0.2−0.3 eV estimated for the experimental D_0 values, we believe the latter D_0(Fe−C) and D_0(Fe^+−C) predictions are more accurate than those obtained using the theoretical CCSD(T)/aug-cc-pV5Z harmonic frequencies.

The theoretical values of D_0(Fe−C) and D_0(Fe^+−C) have also been reported by Tzeli and Mavridis using the MRCI methods with different size basis sets.[9,10] Their best estimate to the dissociation energy without correction of the ZPVE for FeC, D_e(Fe−C), obtained at the C-MRCI+Q level included with core−valence correlation effects, Davidson correction, and scalar relativistic effect is 88.1 kcal/mol (or 3.82 eV). This D_e(Fe−C) value may be converted into D_0(Fe−C) = 86.9 kcal/mol (or 3.77 eV) by subtracting the corresponding ZPVE ($\omega_e/2$ = 438.5 cm^{-1}) obtained at the C-MRCI+Q level. The D_0(Fe^+−C) at the C-MRCI+Q level included with core−valence correlation effects, Davidson correction, and scalar relativistic effect is 92 kcal/mol (or 4.0 eV).[10] While our predicted D_0(Fe^+−C) value at the coupled cluster level is similar to this D_0(Fe^+−C) value obtained with the C-MRCI+Q theory, our CCSDTQ(Full)/CBS D_0(Fe−C) value is similar with the C-MRCI+Q ones. Compared with the experimental values of D_0(Fe−C) and D_0(Fe^+−C), our CCSDTQ(Full)/CBS predictions are in better agreement with experiment measurements. Nevertheless, the C-MRCI+Q D_0 predictions calculated by Tzeli and Mavridis still fall within the uncertainty range of the experimental values. The agreement between our CCSDTQ(Full)/CBS predictions with the experimental values and with the MRCI-based theoretical predictions suggests that the single-reference based coupled cluster theory (with excitations up to full quadruple) is capable of yielding reliable thermochemical predictions for transition metal containing molecules with significant multireference characters.

As pointed out above, using the highly precise experimental IE(FeC) and IE(Fe) values and eq 4, we can arrive at the experimental value of D_0(Fe^+−C) − D_0(Fe−C) = 0.3094 ± 0.0001 eV. The latter value is compared to the present CCSDTQ(Full)/CBS prediction of 0.334 eV and the C-MRCI+Q value of ≈0.2 eV for D_0(Fe^+−C) − D$_0$(Fe−C). This comparison again indicates that the D_0 values obtained by the present CCSDTQ(Full)/CBS calculations are more accurate than those of the C-MRCI+Q calculations.

D. Heats of Formation for FeC and FeC^+. Two values for $\Delta H°_{f0}(FeC^+)$ have been determined based on the ion photodissociation study by Hettich and Freiser and the ion appearance energy measurement by Angeli et al.[43,47] These two $\Delta H°_{f0}(FeC^+)$ values have large uncertainties and are found to differ by more than 34 kJ/mol. Using the D_0(Fe^+−C) value of 94 ± 7 kcal/mol and the known values of $\Delta H°_{f0}(Fe^+)$ and $\Delta H°_{f0}$(C), Hettich and Freiser derived a value of 358 ± 7 kcal/mol (or 1497 ± 29 kJ/mol) for $\Delta H°_{f0}(FeC^+)$, which is about 5 kJ/mol above our CCSDTQ(Full)/CBS prediction (1492.5 kJ/mol) shown in Table 3. Similarly, another experimental value of $\Delta H°_{f0}(FeC^+)$ = 366.0 ± 6 kcal/mol (or 1531.1 ± 25 kJ/mol) was deduced using the D_0(Fe^+−C) value of 84.2 ± 4.1 kcal/mol determined from the appearance threshold measurement by Angeli et al.[47] The latter D_0(Fe^+−C) value is larger than our CCSDTQ(Full)/CBS prediction by almost +40 kJ/mol. As we suggested above that the D_0(Fe^+−C) value of 3.7 ± 0.2 eV deduced from the appearance energy measurement of FeC^+ from $Fe(CO)_5$ by Angeli et al. is likely too low, it is logical to find the $\Delta H°_{f0}(FeC^+)$ value deduced from this bond energy to be too high, given that the experimental values for $\Delta H°_{f0}(Fe^+)$ and $\Delta H°_{f0}$(C) are known precisely. In view of the excellent agreement between our theoretical predictions and experimental measurements on the IE(FeC) and D_0(Fe^+−C), our current theoretical value of $\Delta H°_{f0}(FeC^+)$ = 1492.5 kJ/mol strongly suggests that the experimental value of $\Delta H°_{f0}(FeC^+)$ = 1497 ± 29 kJ/mol obtained by Hettich and Freiser is more reliable. As a result, the $\Delta H°_{f0}$($\Delta H°_{f298}$) values of 762.6 (765.9)/1492.5 (1495.8) kJ/mol for FeC/FeC^+ predicted at the CCSDTQ(Full)/CBS level should constitute a reliable set of thermochemical data. If the experimental harmonic vibrational frequencies of the FeC and FeC^+ are used for the ZPVE and thermal corrections of the $\Delta H°_f$ predictions, the $\Delta H°_{f0}$($\Delta H°_{f298}$) values for FeC/FeC^+ become 760.8 (764.2)/1490.6 (1493.9) kJ/mol. Although these values are only a couple of kJ/mol off the

TABLE 3: Individual Energy Contributions to the CCSDTQ(Full)/CBS Atomization Energies and $\Delta H°_{f0}/\Delta H°_{f298}$ Values for FeC and FeC^{+a}

		FeC	FeC^+
$\Delta E_{\text{extrapolated CBS}}{}^{b}$	wCTQ5	363.8	−352.7
	wCQ5	366.6	−349.9
	average	365.2	−351.3
$\Delta E_{CV}{}^{c}$	(T) → T	−0.6	−1.4
$\Delta E_{ZPVE}{}^{d}$		−7.0	−7.5
		-5.2^{e}	-5.6^{e}
$\Delta E_{SO}{}^{f}$		−4.7	−1.0
$\Delta E_{SR}{}^{g}$	CCSD(T)	−8.5	−22.7
	(T) → T	0.1	0.0
	T → Q	0.0	0.6
	subtotal	−8.4	−22.1
$\Delta E_{HOC}{}^{h}$	(T) → T	−15.7	−14.5
	T → Q	33.8	30.5
	subtotal	18.1	16.0
CCSDTQ(Full)/CBS ΣD_0 [I]		362.6	−367.3
		364.4^{e}	-365.4^{e}
CCSDTQ(Full)/CBS $\Delta H°_{f0}{}^{j}$		762.6	1492.5
		760.8^{e}	1490.6^{e}
experimental $\Delta H°_{f0}$		764 ± 29^{k}	1497 ± 29^{k}
		798.5 ± 25^{l}	1531.1 ± 25^{l}
CCSDTQ(Full)/CBS $\Delta H°_{f298}{}^{m}$		765.9	1495.8
		764.2^{e}	1493.9^{e}

[a] All quantities and energy differences are in kJ/mol. [b] Extrapolated from the core and valence correlation energies using eqs 1 and 2 with the aug-cc-pwCV[T-5]Z and aug-cc-pwCV[Q,5]Z basis sets, respectively. [c] Core−valence electronic correlation obtained as the energy difference between CCSD(T) and CCSDT levels using the cc-pwCVTZ basis set. [d] Based on the harmonic vibrational frequencies at the CCSD(T)/aug-cc-pV5Z level. [e] Values obtained using the experimental vibrational frequencies of FeC/FeC^+ for ZPVE corrections. [f] Spin−orbit coupling obtained at the MRCI level with the uncontracted cc-pVTZ basis set. [g] Scalar relativistic effect calculated at the CCSD(T)/aug-cc-pV5Z-DK, CCSDT/aug-cc-pVQZ-DK, and CCSDTQ/cc-pVTZ-DK levels. [h] Higher-order effect calculated at the CCSDT/aug-cc-pVQZ and CCSDTQ/cc-pVTZ levels. [I] $\Sigma D_0 = \Delta E_{\text{extrapolated CBS}} + \Delta E_{CV} + \Delta E_{ZPVE} + \Delta E_{SO} + \Delta E_{SR} + \Delta E_{HOC}$. [j] $\Delta H°_{f0}$ is the sum of ΣD_0 and the experimental $\Delta H°_{f0}(C)$ and $\Delta H°_{f0}(Fe)$ values. [k] The $\Delta H°_{f0}(FeC^+)$ value is from ref 43. The $\Delta H°_{f0}(FeC)$ value is deduced from the $\Delta H°_{f0}(FeC^+) = 1497 \pm 29$ kJ/mol and IE(FeC) = 7.59318 ± 0.00006 eV. [l] The $\Delta H°_{f0}(FeC^+)$ value is from ref 47. The $\Delta H°_{f0}(FeC)$ values is deduced from the $\Delta H°_{f0}(FeC^+) = 1531.1 \pm 25$ kJ/mol and IE(FeC) = 7.59318 ± 0.00006 eV. [m] $\Delta H°_{f298}$ is the sum of ΣD_0, thermal and enthalpy corrections, and experimental $\Delta H°_{f298}(C)$ and $\Delta H°_{f298}(Fe)$ values.

CCSDTQ(Full)/CBS values based on the theoretical harmonic frequencies, they are expected to be more accurate predictions.

IV. Conclusion

We have performed high-level theoretical predictions for the spectroscopic and energetic properties of FeC/FeC^+ at the coupled cluster level using the correlation consistent basis sets. The calculations involve approximation to the complete basis set (CBS) limit at the coupled cluster level up to quadruple excitations. The zero-point vibrational energy correction, the core−valence electronic corrections (up to CCSDT level), spin−orbit couplings, and relativistic effects (up to CCSDTQ level) are taken into account. While the UHF-UCCSD(T) harmonic frequencies for FeC/FeC^+ are found to be in agreement with the experimental measurements, the ROHF-UCCSD(T) yields significantly higher harmonic frequency predictions for FeC/FeC^+. The predicted IE(FeC) of 7.565 eV effectively at the CCSDTQ(Full)/CBS level is 30 meV below the experimental value of 7.59318 ± 0.00006 eV determined from the recent two-color laser PFI-PE measurement. Comparing the predicted D_0 values with the available experimental data, we conclude that the experimental $D_0(Fe^+{-}C)$ (4.1 ± 0.3 eV) and $D_0(Fe{-}C)$ (3.8 ± 0.3 eV) determined by the early ion photodissociation study are more reliable than those deduced based on the dissociative photoionization measurement. Likewise, our CCSDTQ(Full)/CBS prediction on the $\Delta H°_{f0}(FeC^+) = 1492.5$ kJ/mol is also in better agreement with the experimental value (1497 ± 29 kJ/mol) derived from the $D_0(Fe^+{-}C)$ value by the ion photodissociation experiment of Hettich and Freiser. For accurate predictions of the D_0 and $\Delta H°_f$ values for FeC/FeC^+, we found that the energetic contributions due to relativistic effect and the higher-order corrections beyond the CCSD(T) theory are highly critical. On the basis of the comparisons between the CCSDTQ(Full)/CBS predictions and the previous C-MRCI+Q calculations, the single-reference based CCSDTQ(Full)/CBS method in general performs in par with the multireference based theoretical theory. The comparison between the theoretical and experimental IE(FeC) and D_0 values in the present study supports the conclusion that the single-reference CCSDTQ(Full)/CBS method is capable of giving reliable energetic predictions for transition metal containing diatomic molecules with multireference characters. We recommend the predicted D_0 values [$D_0(Fe{-}C) = 3.778$ eV and $D_0(Fe^+{-}C) = 4.112$ eV] and $\Delta H°_{f0}/\Delta H°_{f298}$ values [$\Delta H°_{f0}(FeC)/\Delta H°_{f298}(FeC) = 760.8/764.2$ kJ/mol and $\Delta H°_{f0}(FeC^+)/\Delta H°_{f298}(FeC^+) = 1490.6/1493.9$ kJ/mol] based on the ZPVE corrections obtained from the experimental vibrational frequencies of FeC/FeC^+. As these D_0 and $\Delta H°_{f0}/\Delta H°_{f298}$ values have not been experimentally determined with high precision, our theoretical predictions presented here should be taken as a reliable set of thermochemical data.

Acknowledgment. The authors are grateful to Professor W. K. Li for helpful comments on the manuscript. This work was supported by NSF Grant No. CHE 0517871. Partial support by the DOE Contract No. DE-FG02-02ER15306, the AFOSR Grant No. FA9550-06-1-0073, and the NASA Grant No. 07-PATM07-0012 is also gratefully acknowledged. The work described in this article was supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. CityU 101308 K.C.L.).

References and Notes

(1) Harrison, J. F. *Chem. Rev.* **2000**, *100*, 679. references therein.

(2) Merer, A. J. *Annu. Rev. Phys. Chem.* **1989**, *40*, 407. references therein.

(3) Balfour, W. J.; Cao, J.; Prasad, C. V. V.; Qian, C. X. W. *J. Chem. Phys.* **1995**, *103*, 4046.

(4) Brugh, D. J.; Morse, M. D. *J. Chem. Phys.* **1997**, *107*, 9772.

(5) Harrington, J.; Weisshaar, J. C. *J. Chem. Phys.* **1992**, *97*, 280.

(6) Linton, C.; Simard, B.; Loock, H. P.; Wallin, S.; Rothschopf, G. K.; Gunion, R. F.; Morse, M. D.; Armentrout, P. B. *J. Chem. Phys.* **1999**, *111*, 5017.

(7) Loock, H.; Simard, B.; Wallen, S.; Linton, C. *J. Chem. Phys.* **1998**, *109*, 8980.

(8) Chang, Y.-C.; Lam, C.-S.; Reed, B.; Lau, K.-C.; Liou, H. T.; Ng, C. Y. *J. Phys. Chem. A* **2009**, *113*, 4242.

(9) Tzeli, D.; Mavridis, A. *J. Chem. Phys.* **2002**, *116*, 4901.

(10) Tzeli, D.; Mavridis, A. *J. Phys. Chem. A* **2005**, *109*, 9249.

(11) Raghavachari, K.; Curtiss, L. A. In *Understanding Chemical Reactivity: Quantum-Mechanical Prediction of Thermochemical Data*; Ciosolwski, J. , Ed.; Kluwer Academic Publishers: New York, 2001; Vol. 22, pp 67−95 andreferences cited therein.

(12) Martin, J. M. L.; Parthiban, S. In *Understanding Chemical Reactivity: Quantum-Mechanical Prediction of Thermochemical Data*; Ciosolwski, J. , Ed.; Kluwer Academic Publishers: New York, 2001; Vol. 22, pp 31−62 andreferences cited therein.

(13) Lau, K.-C.; Ng, C. Y. *Acc. Chem. Res.* **2006**, *39*, 823.

(14) Lau, K.-C.; Ng, C. Y. *J. Chem. Phys.* **2005**, *122*, 224310.

(15) Lau, K.-C.; Ng, C. Y. *J. Chem. Phys.* **2006**, *124*, 044323.

(16) Lau, K.-C.; Ng, C. Y. *Chin. J. Chem. Phys.* **2006**, *19*, 29.

(17) Lau, K.-C.; Zheng, W.; Wong, N.-B.; Li, W.-K. *J. Chem. Phys.* **2007**, *127*, 154302.

(18) Balabanova, N. B.; Peterson, K. A. *J. Chem. Phys.* **2005**, *123*, 064107.

(19) (a) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007. (b) Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

(20) Williams, T. Gavin.; DeYonker, N. J.; Wilson, A. K *J. Chem. Phys.* **2008**, *128*, 044101.

(21) DeYonker, N. J.; Peterson, K. A.; Steyl, G.; Wilson, A. K.; Cundari, T. R. *J. Phys. Chem. A* **2007**, *111*, 11269.

(22) Balabanov, N. B.; Peterson, K. A. *J. Chem. Phys.* **2006**, *125*, 074110.

(23) Watts, J. D.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 8718.

(24) Rittby, M.; Bartlett, R. J. *J. Phys. Chem.* **1998**, *92*, 3033.

(25) Hampel, C.; Peterson, K. A.; Werner, H. J. *Chem. Phys. Lett.* **1992**, *190*, 1.

(26) Deegan, M. J. O.; Knowles, P. J. *Chem. Phys. Lett.* **1994**, *227*, 321.

(27) Knowles, P. J.; Hampel, C.; Werner, H. J. *J. Chem. Phys.* **1993**, *99*, 5219.

(28) Peterson, K. A.; Dunning, T. H. Jr. *J. Chem. Phys.* **2002**, *117*, 10548.

(29) Peterson, K. A.; Woon, D. E.; Dunning, T. H. Jr. *J. Chem. Phys.* **1994**, *100*, 7410.

(30) Helgaker, T.; Klopper, W.; Koch, H.; Nago, J. *J. Chem. Phys.* **1996**, *106*, 9639.

(31) Halkier, A.; Helgaker, T.; Jorgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. *Chem. Phys. Lett.* **1998**, *286*, 243.

(32) Douglas, M.; Kroll, N. M. *Ann. Phys.* **1974**, *82*, 89.

(33) Jansen, G.; Hess, B. A. *Phys. Rev. A* **1989**, *39*, 6016.

(34) de Jong, W. A.; Harrison, R. J.; Dixon, D. A. *J. Chem. Phys.* **2001**, *114*, 48.

(35) Berning, A.; Schweizer, M.; Werner, H.-J.; Knowles, P. J.; Palmieri, P. *Mol. Phys.* **2000**, *98*, 1823.

(36) Moore, C. E. Atomic Energy Levels; Natational Bureau of Standards (U.S.) Circular No. 467; U.S. Government Printing Office: Washington, DC, 1949.

(37) Werner, H.-J.; Knowles, P. J. ; Lindh, R. ; Manby, F. R. ; Schütz, M. ; Celani, P. ; Korona, T. ; Mitrushenkov, A. ; Rauhut, G. ; Adler, T. B. ; Amos, R. D. , Bernhardsson A. ; Berning, A. ; Cooper, D. L. ; Deegan, M. J. O. ; Dobbyn, A. J. ; Eckert, F. ; Goll, E. ; Hampel, C. ; Hetzer, G. ; Hrenar, T. ; Knizia, G. ; Köppl, C. ; Liu, Y. ; Lloyd, A. W. ; Mata, R. A., May, A. J. ; McNicholas, S. J. ; Meyer, W. ; Mura, M. E. ; Nicklass, A. ; Palmieri, P. ; Pflüger, K. ; Pitzer, R. ; Reiher, M. ; Schumann, U. ; Stoll, H. ; Stone, A. J. ; Tarroni, R. ; Thorsteinsson, T. ; Wang, M. ; Wolf, A. MOLPRO is a package of ab initio programs.

(38) MRCC, a string-based quantum chemical program suite written by M. Kállay. See also Kállay, M.; Surján, P. R. *J. Chem. Phys.* **2001**, *115*, 2945, as well as www.mrcc.hu..

(39) Curtiss, L. A.; Raghavachari, K. P.; Redfern, C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.

(40) 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. .

(41) Aiuchi, K.; Tsuji, K.; Shibuya, K. *Chem. Phys. Lett.* **1999**, *309*, 229.

(42) See for example refs 18 and 20.

(43) Hettich, R. L.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 2537.

(44) NIST Atomic Spectra Database, version 3.1.5, 2008, http://physics.nist.gov/asd3.

(45) Kai-Chung Lau, Yih-Chung Chang, Xiaoyu Shi, Ng C. Y. To be published.

(46) Yih-Chung Chang, Xiaoyu Shi, Kai-Chung Lau, Ng C. Y. To be published.

(47) Angeli, C.; Berthier, G.; Rolando, C.; Sablier, M.; Alcaraz, C.; Dutuit, O. *J. Phys. Chem. A* **1997**, *101*, 7907.

JP903218H