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High-level *ab initio* predictions for the ionization energy, bond dissociation energies, and heats of formation of cobalt carbide (CoC) and its cation (CoC⁺)

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High-level *ab initio* predictions for the ionization energy, bond dissociation energies, and heats of formation of cobalt carbide (CoC) and its cation (CoC⁺)

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The ionization energy (IE) of CoC and the 0 K bond dissociation energies (D_0) and the heats of formation at 0 K (ΔH°_{f0}) and 298 K (ΔH°_{f298}) for CoC and CoC⁺ are predicted by the wavefunction based coupled-cluster theory with single, double, triple and quadruple excitations (CCSDTQ) and complete basis set (CBS) approach. The CCSDTQ/CBS calculations presented here involve the approximation to the CBS limit at the coupled cluster level up to full quadruple excitations along with the zero-point vibrational energy, high-order correlation, core-valence (CV) electronic, spin-orbit coupling, and scalar relativistic effect corrections. The present calculations provide the correct symmetry, $^1\Sigma^+$, for the ground state of CoC⁺. The CCSDTQ/CBS IE(CoC) = 7.740 eV is found in good agreement with the experimental IE value of 7.73467 ± 0.00007 eV, determined in a two-color laser photoion and pulsed field ionization-photoelectron study. This work together with the previous experimental and theoretical investigations support the conclusion that the CCSDTQ/CBS method is capable of providing reliable IE predictions for 3d-transition metal carbides, such as FeC, CoC, and NiC. Among the single-reference based coupled-cluster methods and multi-reference configuration interaction (MRCI) approach, the CCSDTQ and MRCI methods give the best predictions to the harmonic frequencies ω_e (ω_e^+) = 956 (992) and 976 (1004) cm⁻¹ and the bond lengths r_e (r_e^+) = 1.560 (1.528) and 1.550 (1.522) Å, respectively, for CoC (CoC⁺) in comparison with the experimental values. The CCSDTQ/CBS calculations give the prediction of $D_0(\text{Co}^+-\text{C}) - D_0(\text{Co}-\text{C}) = 0.175$ eV, which is also consistent with the experimental determination of 0.14630 ± 0.00014 eV. The theoretical results show that the CV and valence-valence electronic correlations beyond CCSD(T) wavefunction and the relativistic effect make significant contributions to the calculated thermochemical properties of CoC/CoC⁺. For the experimental D_0 and ΔH°_{f0} values of CoC/CoC⁺, which are not known experimentally, we recommend the following CCSDTQ/CBS predictions: $\Delta H^\circ_{f0}(\text{CoC}) = 775.7$ kJ/mol and $\Delta H^\circ_{f0}(\text{CoC}^+) = 1522.5$ kJ/mol, $\Delta H^\circ_{f298}(\text{CoC}) = 779.2$ kJ/mol and $\Delta H^\circ_{f298}(\text{CoC}^+) = 1526.0$ kJ/mol. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4792718>]

I. INTRODUCTION

Transition metal (M)-containing molecules have been playing more and more important roles in various scientific areas, including catalytic and biological processes, material chemistry, astrophysics, to name just a few.^{1,2} In contrast to their versatility, their experimental characterization³⁻⁹ and theoretical studies¹⁰⁻¹⁶ are relatively deficient even for prototypical systems such as diatomic transition metal oxides, nitrides, carbides, and hydrides (MX, X = O, N, C, and H). The presence of the 3d-electrons and hence the manifolds of low-lying electronic states create obstacles in both spectroscopic and theoretical investigations.

To confront the aforementioned difficulties computationally, multi-reference (MR) calculation has been recommended to be one of the viable methods.¹¹⁻¹³ Due to the recent advances in quantum theoretical methodologies, sophisticated

electron correlation and correction effects have become possible. Perturbative treatments¹⁷ and variational methods¹¹⁻¹³ have been applied to the multiconfiguration wavefunction which is further corrected for relativistic^{18,19} and spin-orbit effects involving multiple electronic states. For instance, the contemporary multi-reference configuration interaction (MRCI) methods are now ranked as the state-of-the-art *ab initio* quantum chemical procedures for structural and energetic calculations for M-containing species, and are expected to be very reliable.¹¹⁻¹³

Recently, we have initiated a highly accurate spectroscopic and energetic study on a series of 3d-transition metal carbides (MC) by mean of two-color laser photoionization efficiency (PIE) and pulsed field ionization-photoelectron (PFI-PE) measurements.^{20,21} From the investigations on FeC and NiC, the ionization energies (IEs) of the carbides and other spectroscopic constants of the respective cations have been determined with unprecedented accuracy.^{20,21} However, in comparison with the IE values predicted by the MRCI

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method with Davidson correction (MRCI+Q) and semi-core electron correlation (C-MRCI+Q),^{11,22} a disagreement of up to 0.5 eV has been observed. Such a disagreement has recently motivated the revisit of the bond dissociation energies (D_0) of FeC/FeC⁺ at the MRCI+Q level by Tzeli and Mavridis.^{11(c)} The high accuracy demonstrated by the CCSDTQ/complete basis set (CBS) approach in the thermochemical predictions of a series of hydrocarbon radicals²³ led us to use this procedure to investigate the FeC/FeC⁺ and NiC/NiC⁺ systems.^{22,24} The CCSDTQ/CBS calculations involve the approximation to the CBS limit at the coupled cluster level up to quadruple excitations. Various corrections, including zero-point vibrational energy (ZPVE) corrections, high-order correction (HOC) beyond the CCSD(T) wavefunction, the core-valence (CV) electronic corrections (up to CCSDT level), and the spin-orbit (SO) and scalar-relativistic (SR) corrections (up to CCSDTQ level) are taken into account. In both theoretical studies, the CCSDTQ/CBS predictions are accurate, with a discrepancy of less than 30 meV to the experimental values. The comparison between the theoretical and experimental values in the previous studies^{22,24} suggests that the CCSDTQ/CBS method is capable of giving reliable IE and D_0 predictions for ground state $3d$ -transition metal-containing diatomics. As the CCSDTQ/CBS procedure is a single reference method, the good agreement on $3d$ -transition metal-molecules, potentially having multi-reference character, might be fortuitous. Hence, additional benchmarking of the CCSDTQ/CBS procedure is clearly desirable.

In the companion article, we report a two-color laser PIE and PFI-PE experiment on CoC, yielding well-resolved rotational transitions for the $v^+ = 0$ and 1 vibrational bands of the CoC⁺($X^1\Sigma^+$) ground state.²⁵ The rotational assignment of these PFI-PE spectra has made possible the direct determination of the IE(CoC) = 7.73467 ± 0.00007 eV and the vibrational spacing of 973.1 ± 0.6 cm⁻¹ between the $v^+ = 0$ and 1 vibrational levels of CoC⁺($X^1\Sigma^+$). Here, we report the CCSDTQ/CBS calculations of IE(CoC), $D_0(\text{Co}^+-\text{C})$, $D_0(\text{Co}-\text{C})$, $\Delta H_f(\text{CoC})$, $\Delta H_f(\text{CoC}^+)$, vibrational frequencies (ω_e and ω_e^+), and bond lengths (r_e and r_e^+) of the CoC($X^2\Sigma^+$) and CoC⁺($X^1\Sigma^+$) ground states. In particular, the theoretical results for IE(CoC), ω_e , ω_e^+ , r_e , and r_e^+ are compared and benchmarked with the experimental measurements. We have also obtained density functional theory (DFT) results in order to compare with those from the CCSDTQ/CBS calculations. Based on the comparisons, critical assessments of the reliability and accuracy of the single-reference and multi-reference based theoretical methods on cobalt carbide and its cation are made. The MRCI+Q predictions on bond length and ω_e for the ground state (and excited states) of CoC have been reported previously,¹³ while the relevant theoretical predictions on the CoC⁺ are reported for the first time.

II. THEORETICAL METHODS

In the coupled cluster calculations of the CCSDTQ/CBS procedure, we have chosen to use the partially unrestricted implementation, conventionally labeled as ROHF-UCCSD(T). This method is based on restricted open-shell

Hartree-Fock (ROHF) orbitals and relaxes the spin restriction throughout the calculation.^{26,27}

A. The CCSDTQ/CBS calculations involve the approximation to the CBS limit at the CCSD(T) level of theory. The ground state structures of the CoC ($X^2\Sigma^+$) and CoC⁺ ($X^1\Sigma^+$) have been optimized at the CCSD(T) level, proceeding from aug-cc-pwCVTZ, to aug-cc-pwCVQZ, to aug-cc-pwCV5Z,^{28,29} basis sets. Besides the valence $2s2p$ electrons on carbon and $3d4s$ electrons on Co, the geometry optimizations also correlate the core $1s$ electrons on carbon and outer-core $3s3p$ electrons on Co. The $1s2s2p$ electrons on Co are kept frozen and uncorrelated. The total CCSD(T) energies are used to extrapolate the CBS energies ($E_{\text{extrapolated CBS}}$) by the following two schemes:

(i) A three-point extrapolation scheme³⁰ using the mixed exponential/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. The CBS energies extrapolated using Eq. (1) is denoted as CBS_{wTQ5}.

(ii) A two-point extrapolation scheme^{31,32} using the simple power function involving the reciprocal of X ,

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

where $X = 4$ and 5 for aug-cc-pwCVQZ and aug-cc-pwCV5Z, respectively. The extrapolated CBS energies obtained from Eq. (2) are denoted as CBS_{wQ5}. Previous calculations on FeC/FeC⁺²⁴ and NiC/NiC⁺²² and other main-group molecules²³ reveal that the difference of extrapolated energetics between the two-point and three-point extrapolation schemes is typically small, thus an average of the two extrapolated energies are adopted.

B. The HOC 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 and CCSDT energies. The HOC for CoC/CoC⁺ is taken as

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

C. The SR energy is computed using the spin-free, one-electron Douglas-Kroll-Hess (DKH) Hamiltonian.^{18,19} The calculations are done with the DKH-contracted aug-cc-pV5Z-DK basis sets^{29,33} at the CCSD(T) level. The SR energetic contributions (E_{SR}) are taken as the difference 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 are also 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 in the respective CCSDT and CCSDTQ calculations.

- D. 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 difference between CCSD(T) and CCSDT energies with the aug-cc-pwCVTZ basis set.^{28,29} The core $1s$ electrons on carbon and outer-core $3s3p$ electrons on Co are correlated.
- E. The molecular spin-orbit coupling (E_{SO}) of the CoC are computed by first-order perturbation theory. The calculations use the uncontracted aug-cc-pVTZ basis set including the s , p , d , and f functions on Co and the s , p , d functions on C. Spin-orbit matrix elements are computed among the components of the CoC state using the internally contracted MRCI wavefunction.³⁴ The $2s2p$ electrons on C and the $3d4s$ electrons on Co are included in the active space. The atomic spin-orbit correction of Co/Co⁺ are done in a similar manner. The atomic spin-orbit correction (0.37 kJ/mol) for carbon is directly taken from the experimental excitation energies tabulated by Moore.³⁵ The harmonic vibrational frequencies at the CCSDTQ/cc-pVTZ level are used for the zero-point vibrational energy corrections (ΔE_{ZPVE}).

In the present work, all the CCSD(T) single-point energy and correlation contribution calculations are performed using the MOLPRO 2010.1³⁶ program and the CCSDT/CCSDTQ calculations are done with the string-based many-body MRCC program³⁷ interfaced with MOLRPO. The ΔH°_{f0} and ΔH°_{f298} values for CoC and CoC⁺ were evaluated using the atomization scheme³⁸ and the following experimental thermochemical data (in kJ/mol):³⁹ $\Delta H^\circ_{f0}(C) = 711.2$, $\Delta H^\circ_{f0}(Co) = 425.1$, $\Delta H^\circ_{f298}(C) = 716.7$, and $\Delta H^\circ_{f298}(Co) = 426.7$. The 298 K thermal and enthalpy corrections to 0 K energies for elements and compounds are estimated using the methods adopted from Ref. 38.

III. RESULTS AND DISCUSSION

At the single-reference CCSD(T) level, the ground electronic state CoC is predicted to have the $^2\Sigma^+$ symmetry. Based on the previous experimental determinations^{6,40,41} and multi-reference based *ab initio* calculations,¹³ the ground state of CoC has a main configuration of $\dots 7\sigma^2 8\sigma^2 3\pi^4 1\delta^4 9\sigma^1$. The valence electrons of CoC consist of the $4s^2 3d^7$ electrons of Co and the $2s^2 2p^2$ electrons of C. The nonbonding 9σ orbital is dominated by the Co($4s$) atomic orbital. The first ionization of CoC would involve the removal of an electron from 9σ orbital, resulting in a $^1\Sigma^+$ ground state for CoC⁺. The symmetry of the CoC⁺($X^1\Sigma^+$) ground state is confirmed by the rotational band observed in the PFI-PE spectrum of cobalt carbide.²⁵ The triple bond (and its length) in CoC is practically unaffected by the adiabatic ionization process. We have examined the leading

configurations of the ground state CoC and CoC⁺ in the complete active space self-consistent field (CASSCF) wavefunctions, the coefficients of the dominant configurations are found to be 0.84 and 0.88 for CoC and CoC⁺, respectively, indicating that both the ground states of CoC and CoC⁺ have considerable multi-reference character.

A. Equilibrium bond length and harmonic vibration frequency of CoC and CoC⁺

The bond lengths r_e (r_e^+) and harmonic vibrational frequencies ω_e (ω_e^+) of CoC($X^2\Sigma^+$) [CoC⁺($X^1\Sigma^+$)] at the CCSD(T)/aug-cc-pVXZ, CCSD(T)/aug-cc-pwCVXZ, CCSDT/aug-cc-pVTZ, CCSDTQ/cc-pVTZ, and B3LYP/aug-cc-pVXZ levels are summarized in Table I. The calculations at the CCSD(T)/aug-cc-pwCVXZ level have included the core-valence and valence-valence electronic correlations for the $3s3p3d4s$ (Co) and $1s2s2p$ (C) electrons. The experimental results for the neutral^{40–42} and the cation²⁵ are included. The CCSD(T) predicted r_e values for CoC are ranging from 1.548 to 1.545 Å with successively increasing basis set size from aug-cc-pVTZ to aug-cc-pV5Z. Once the core-valence correlation effect is included, the bond lengths are slightly reduced by about 0.003 Å. By proceeding from CCSDT/aug-cc-pVTZ to CCSDTQ/cc-pVTZ level, the r_e of CoC is increased from 1.543 to 1.560 Å, fortuitously, the CCSDTQ result is essentially identical to the experimental value. The CCSD(T), CCSDT, and MRCI-based r_e values for CoC are shorter than the experimental bond length of 1.5612⁴¹ and 1.5601⁴² by 0.01–0.02 Å.

In the companion article,²⁵ we have reported the experimental values of $r_e^+ = 1.534$ Å and $\omega_e^+ = 985.6 \pm 0.6$ cm⁻¹

TABLE I. The bond length r_e (r_e^+) in Å and harmonic vibrational frequency ω_e (ω_e^+) in cm⁻¹ for CoC($X^2\Sigma^+$) [CoC⁺($X^1\Sigma^+$)] predicted at the CCSD(T), CCSDT, CCSDTQ, MRCI, and B3LYP using aug-cc-p(w)VXZ levels, where X = T, Q, and 5.

	CoC ($^2\Sigma^+$)		CoC ⁺ ($^1\Sigma^+$)	
	r_e	ω_e	r_e^+	ω_e^+
CCSD(T)/aug-cc-pVTZ	1.548	1314	1.504	1080
CCSD(T)/aug-cc-pVQZ	1.546	1332	1.499	1095
CCSD(T)/aug-cc-pV5Z	1.545	1342	1.497	1098
CCSD(T)/aug-cc-pwCVTZ ^a	1.545	1386	1.496	1133
CCSD(T)/aug-cc-pwCVQZ ^a	1.543	1401	1.492	1141
CCSD(T)/aug-cc-pwCV5Z ^a	1.543	1408	1.490	1145
CCSDT/aug-cc-pVTZ	1.543	981	1.513	1019
CCSDTQ/cc-pVTZ	1.560	956	1.528	992
MRCI/aug-cc-pwCV5Z ^b	1.550	976	1.522	1004
B3LYP/aug-cc-pVTZ	1.510	868	1.472	1166
B3LYP/aug-cc-pVQZ	1.508	919	1.470	1166
B3LYP/aug-cc-pV5Z	1.508	922	1.470	1166
Experimental	1.5612 ^c	955 ^c	1.534 ^d	985.6 ± 0.6 ^d
	1.5601 ^e			

^aCorrelated with the $3s3p3d4s$ (Co) and $1s2s2p$ (C) electrons.

^bActive space includes 13 electrons [$4s^2 3d^7$ (Co) + $2s^2 2p^2$ (C)] in 10 orbitals [five $3d$ (Co) + one $4s$ (Co) + one $2s$ (C) + three $2p$ (C)] for CoC and 12 electrons in 10 orbitals for CoC⁺. Outer-core $3s^2 3p^6$ (Co) electrons are included in the CI procedure.

^cReference 41.

^dDetermined from the companion article, Ref. 25.

^eReference 42.

for the ground state of CoC^+ . The bond distance of CoC is almost unchanged upon ionization, consistent with the CASSCF bonding analysis¹³ that the 9σ orbital is mostly non-bonding in nature. The CCSD(T) predicted r_e^+ values for CoC^+ are found shorter than the experimental bond length of 1.534 Å determined from the PFI-PE study by about 0.035 Å. The CCSDT method yields a longer r_e^+ value of 1.513 Å for CoC^+ and it is still about 0.02 Å smaller than the experimental r_e^+ . Among the CCSD(T), CCSDT, and CCSDTQ methods, the latter method gives a r_e^+ value of 1.528 Å in good agreement with the experimental r_e^+ value. The MRCI-based r_e^+ of 1.522 Å is in par with the CCSDTQ result but superior to those obtained at CCSD(T) and CCSDT levels.

The CCSD(T) ω_e values of CoC , ranging from 1314 to 1342 cm^{-1} over the three aug-cc-pVXZ basis sets, are badly deviated from the experimental ω_e of 955 cm^{-1} . The experimental ω_e of CoC is deduced using the $\Delta G_{1/2} = 934 \text{ cm}^{-1}$ and $\Delta G_{3/2} = 913 \text{ cm}^{-1}$ values obtained from the vibrational structures in the laser induced fluorescence spectrum of $\text{CoC} (X^2\Sigma^+) \leftarrow \text{CoC} (^2\Pi)$ by Barnes, Merer, and Metha.⁴¹ Inclusion of the core-valence effect at the CCSD(T) level leads to even larger ω_e values (by $\sim 70 \text{ cm}^{-1}$). Similar situation is also found for the CCSD(T) predictions on the ω_e^+ values of CoC^+ . The predicted CCSD(T)/aug-cc-pVXZ (1080–1098 cm^{-1}) and CCSD(T)/aug-cc-pwCVXZ (1133–1145 cm^{-1}) values are much higher than the experimental value of 985.6 cm^{-1} , by over 100 and 150 cm^{-1} , respectively. As in a previous study,²⁴ we found that the CCSD(T) method was unable to give reliable harmonic vibrational frequencies on FeC/FeC^+ and now the same situation arises for CoC/CoC^+ . However, by including the full triplet and triplet/quadruple excitations in the coupled-cluster theory, the CCSDT and CCSDTQ ω_e (ω_e^+) values become 981 (1019) and 956 (992) cm^{-1} , respectively. While the CCSDT ω_e (ω_e^+) values are still larger than the experimental values by 26 (33) cm^{-1} and the CCSDTQ predictions are just 1 (6) cm^{-1} off from the experiments. Thus, the inclusion of full triplet and/or quadruple excitations in the coupled-cluster theory are critical to give the correct harmonic force constant and hence vibrational frequencies of CoC/CoC^+ . The good agreement between the CCSDT/CCSDTQ predictions and experimental values is also observed on the ω_e (ω_e^+) of FeC/FeC^+ .⁴³ Tzeli and Marvidis¹³ have reported a CCSD(T) ω_e value of 1004 cm^{-1} using the CASSCF natural orbitals in the CCSD(T) calculations. This CCSD(T) ω_e value is significantly better than these values (in Table I) using canonical HF orbitals, probably due to the inclusion of nondynamic correlation in the CASSCF wavefunction. The MRCI method also gives very close predictions for ω_e (ω_e^+) = 976 (1004) cm^{-1} to the experimental values and the deviation is 21 (18) cm^{-1} .

The density functional theory has been extensively used for structural and energetic predictions of transition-metal compounds,¹⁰ relevant calculations at the B3LYP/aug-cc-pVXZ levels have been done for CoC/CoC^+ to evaluate the performance of DFT method. The respective r_e/r_e^+ and ω_e/ω_e^+ values, using the aug-cc-pV5Z basis set, are 1.508/1.470 Å and 922/1166 cm^{-1} . Comparing with experiments, the B3LYP predictions underestimate both r_e and r_e^+ by about 0.06 Å. The B3LYP vibrational frequencies

for CoC and CoC^+ deviate from experimental values by -33 cm^{-1} and 183 cm^{-1} , respectively, indicating that the B3LYP method is not reliable for the spectroscopic calculations of CoC/CoC^+ and NiC/NiC^+ .^{22,24} The B3LYP predictions obtained here are very similar to the DFT results by Bauschlicher *et al.*¹⁰

B. Ionization energies of CoC and Co

CoC has many low-lying excited states,¹³ giving rise to its multi-reference character. The first electronically excited state of $\text{CoC} (A^2\Delta)$ is lying above the ground state of $\text{CoC} (X^2\Sigma^+)$ by 2 kcal/mol.⁴¹ It is of great importance to examine whether the single-reference coupled cluster theory can provide reliable energetic predictions for CoC/CoC^+ . The individual energy corrections ($\Delta E_{\text{extrapolated CBS}}$, ΔE_{CV} , ΔE_{ZPVE} , ΔE_{SO} , ΔE_{SR} , and ΔE_{HOC}) for $\text{IE}(\text{CoC})$, $\text{IE}(\text{Co})$, $\text{D}_0(\text{Co}-\text{C})$, and $\text{D}_0(\text{Co}^+-\text{C})$ predictions using the CCSDTQ/CBS method are listed in Table II. The CCSDTQ/CBS $\text{IE}(\text{CoC}) = 7.740 \text{ eV}$ is found to be in excellent agreement with the experimental $\text{IE}(\text{CoC}) = 7.73467 \pm 0.00007 \text{ eV}$ measured from the PFI-PE spectrum of CoC .²⁵ The average of the $\Delta E_{\text{extrapolated CBS}}$ contributions to the $\text{IE}(\text{CoC})$ is 7.585 eV; the ΔE_{ZPVE} correction, based on the CCSDTQ predicted ω_e/ω_e^+ values, is 2 meV. The ΔE_{CV} contribution due to core-valence correlation at the CCSDT level is as large as -19 meV . The relativistic effect from the full triple and quadruple excitations makes a large contribution of 0.148 eV. The higher-order correction, accounting for full triple and quadruple excitations in the coupled-cluster theory, provides a critical amount of 24 meV to the $\text{IE}(\text{CoC})$ value. Putting all the correlation contributions together, we arrive at an $\text{IE}(\text{CoC})$ value of 7.740 eV. Although the CCSDTQ-based harmonic ZPVE correction is close to zero, it is worth pointing out that only the CCSDT and CCSDTQ methods give quantitatively correct ΔE_{ZPVE} correction to $\text{IE}(\text{CoC})$, whereas the CCSD(T) method yields negative ΔE_{ZPVE} corrections, up to -16 meV at the CCSD(T)/aug-cc-pwCV5Z level. In other words, to make a reliable $\text{IE}(\text{CoC})$ prediction, it is necessary to obtain the ZPVE correction at the CCSDT or CCSDTQ levels for CoC/CoC^+ . The CCSDTQ/CBS IE for the ionization transition of $\text{CoC}^+ (X^1\Sigma^+) \leftarrow \text{CoC} (A^2\Delta)$ is 7.71 (without SO coupling) and 7.77 (with SO coupling) eV. This indicates that the low-lying $\text{CoC} (^2\Delta_{5/2})$ state is the SO ground state while the $\text{CoC} (^2\Sigma^+)$ is the lowest-energy J-averaged state of CoC . Similar results on the reversed order of $\text{CoC} (^2\Delta)$ and $\text{CoC} (^2\Sigma^+)$ states were also found by Tzeli and Marvidis¹³ at the MRCI levels at the C-MRCI+Q level (including relativistic effects).

As followed the good agreement in the CCSDTQ/CBS predictions for $\text{IE}(\text{FeC})$ and $\text{IE}(\text{NiC})$ values with the experimental data,^{22,24} it is also pleasing to find that our predicted $\text{IE}(\text{CoC})$ value comes to less than 6 meV above the highly precise experimental value of $7.73467 \pm 0.00007 \text{ eV}$.²⁵ The excellent accord between our prediction and measured value for $\text{IE}(\text{CoC})$ suggests that the nominal single-reference based coupled cluster theory is capable of predicting the $\text{IE}(\text{FeC})$,²⁴ $\text{IE}(\text{CoC})$, and $\text{IE}(\text{NiC})$ ²² values within the chemical accuracy ($\pm 40 \text{ meV}$). Similar to the $\text{IE}(\text{FeC})$ prediction by DFT,²⁴

TABLE II. Individual energy contributions to the CCSDTQ/CBS predictions and B3LYP calculations for the IE(CoC), IE(Co), $D_0(\text{Co-C})$, and $D_0(\text{Co}^+-\text{C})$ values.^a

		IE(CoC)	IE(Co)	$D_0(\text{Co-C})$	$D_0(\text{Co}^+-\text{C})$	$D_0(\text{Co}^+-\text{C}) - D_0(\text{Co-C})$
$\Delta E_{\text{extrapolated CBS}}^b$	wTQ5	7.584	7.408	3.833	3.658	-0.175
	wTQ	7.586	7.396	3.861	3.671	-0.190
	Average	7.585	7.402	3.847	3.665	-0.182
ΔE_{CV}^c	(T) \rightarrow T	-0.019	-0.002	-0.014	0.002	0.016
ΔE_{ZPVE}^d		0.002	...	-0.061	-0.063	-0.002
ΔE_{SO}^e		...	0.012	-0.090	-0.078	0.012
ΔE_{SR}^f	CCSD(T)	0.155	0.484	-0.138	0.191	0.329
	(T) \rightarrow T	-0.009	0.000	-0.008	0.001	0.009
	T \rightarrow Q	0.002	0.000	0.007	0.005	-0.002
	Subtotal	0.148	0.484	-0.139	0.197	0.336
ΔE_{HOC}^g	(T) \rightarrow T	-0.046	0.018	-0.187	-0.123	0.064
	T \rightarrow Q	0.070	0.001	0.381	0.312	-0.069
	Subtotal	0.024	0.019	0.194	0.189	-0.005
CCSDTQ/CBS ^h		7.740	7.915	3.737	3.912	0.175
B3LYP/aug-cc-pVTZ ⁱ		8.07	8.09	3.00	3.02	0.02
Experimental value		7.73467	7.88101	3.75 ± 0.30^l	3.90 ± 0.30^m	0.1463
		$\pm 0.00007^j$	$\pm 0.00012^k$	3.45 ± 0.30^n	3.60 ± 0.30^o	$\pm 0.00012^p$

^aAll quantities and energy differences are in eV.

^bExtrapolated 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.

^cCore-valence electronic correlation obtained as the energy difference between CCSD(T) and CCSDT levels using the aug-cc-pwCVTZ basis set.

^dBased on the harmonic vibrational frequencies at the CCSDTQ/cc-pVTZ level.

^eSpin-orbit coupling obtained at the MRCI level with the uncontracted cc-pwCVTZ basis set.

^fScalar relativistic effect calculated at the CCSD(T)/aug-cc-pV5Z-DK, CCSDT/aug-cc-pVQZ-DK, and CCSDTQ/cc-pVTZ-DK levels.

^gHigher-order effect calculated at the CCSDT/aug-cc-pVQZ and CCSDTQ/cc-pVTZ levels.

^hIE or $D_0 = \Delta E_{\text{extrapolated CBS}} + \Delta E_{\text{CV}} + \Delta E_{\text{ZPVE}} + \Delta E_{\text{SO}} + \Delta E_{\text{SR}} + \Delta E_{\text{HOC}}$.

ⁱThe B3LYP/aug-cc-pVTZ value includes ZPVE and DKH corrections.

^jDetermined from the companion article, Ref. 25.

^kReference 44.

^lDeduced from $D_0(\text{Co}^+-\text{C}) - D_0(\text{Co-C}) = 0.1463 \pm 0.00014$ eV and $D_0(\text{Co}^+-\text{C}) = 3.90 \pm 0.03$.

^mReference 45.

ⁿDeduced from $D_0(\text{Co}^+-\text{C}) - D_0(\text{Co-C}) = 0.1463 \pm 0.00014$ eV and $D_0(\text{Co}^+-\text{C}) = 3.60 \pm 0.03$.

^oReference 46.

^pDeduced from Eq. (4): $D_0(\text{Co}^+-\text{C}) - D_0(\text{Co-C}) = \text{IE}(\text{Co}) - \text{IE}(\text{CoC})$.

the B3LYP/aug-cc-pVTZ level of 8.07 eV (corrected with CCSDTQ ZPVE and relativistic effects) overestimates the experimental value by over 0.3 eV.

The average $\Delta E_{\text{extrapolated CBS}}$ contributions to IE(Co) values based on the two- and three-point extrapolation methods is 7.402 eV. The CV, SO, and HOC corrections are relatively small, with values of -2, 12, and 19 meV, respectively, while the SR correction (0.484 eV) is by far the most significant. After taking all these corrections into account, we arrive at a CCSDTQ/CBS IE(Co) value of 7.915 eV, in very good agreement with the experimental IE(Co) = 7.8810 ± 0.00012 eV.⁴⁴

C. Dissociation energies of the CoC and CoC⁺

On the basis of the cation thermochemical cycle, quantities IE(CoC), IE(Co), $D_0(\text{Co-C})$, and $D_0(\text{Co}^+-\text{C})$ are related by

$$D_0(\text{Co-C}) + \text{IE}(\text{Co}) = D_0(\text{Co}^+-\text{C}) + \text{IE}(\text{CoC}). \quad (4)$$

While the experimental IE(CoC) = 7.73467 ± 0.00007 eV and IE(Co) = 7.8810 ± 0.00012 eV⁴⁴ are accurately known, the $D_0(\text{Co}^+-\text{C})$ and $D_0(\text{Co-C})$ values have not yet been measured accurately. In the literature, there are two experimen-

tal $D_0(\text{Co}^+-\text{C})$ values that are not too far from each other: 3.90 ± 0.30 eV⁴⁵ and 3.60 ± 0.30 .⁴⁶ Using the IE(CoC) and IE(Co) together with the $D_0(\text{Co}^+-\text{C})$ value of 3.90 ± 0.30 eV determined from the early photodissociation measurement of Hettich and Freiser,⁴⁵ we deduce an experimental value of 3.75 ± 0.30 eV for $D_0(\text{Co-C})$. If we use the IE(CoC), IE(Co), and the $D_0(\text{Co}^+-\text{C}) = 3.60 \pm 0.30$ eV, determined in a guided-ion-beam mass spectrometric study on the activation barriers for the reactions $\text{Co} + \text{CD}_4$ and $\text{CoCH}_2^+ + \text{D}_2$ by Armentrout and co-workers,⁴⁶ a lower value of $D_0(\text{Co-C}) = 3.45 \pm 0.30$ eV is obtained. In comparison with these experimental values, our CCSDTQ/CBS predictions of $D_0(\text{Co}^+-\text{C}) = 3.912$ eV and $D_0(\text{Co-C}) = 3.737$ are in excellent agreement with the experimental value of $D_0(\text{Co}^+-\text{C}) = 3.90 \pm 0.30$ eV⁴⁵ and the deduced value of $D_0(\text{Co-C}) = 3.75 \pm 0.30$ eV. As the uncertainty of the experimental values is 300 meV, our CCSDTQ/CBS predictions are still within the error bar of the experimental value of $D_0(\text{Co}^+-\text{C}) = 3.60 \pm 0.30$ eV⁴⁶ and the deduced $D_0(\text{Co-C}) = 3.45 \pm 0.30$ value. The multi-reference based value for $D_0(\text{Co-C})$ is 3.56 eV (82 kcal mol⁻¹ at the MRCI+Q/C4Z with the DKH correction, semi-core $3s^2 3p^6(\text{Co})$ electrons in the CI space and basis set superposition error)¹³ also comes close to both $D_0(\text{Co-C})$

values of 3.75 ± 0.30 and 3.45 ± 0.30 eV. At the B3LYP/aug-cc-pVTZ level, the predicted $D_0(\text{Co-C})$ and $D_0(\text{Co}^+-\text{C})$ values are very similar (difference is 0.02 eV); the B3LYP predictions also support that CoC^+ has a slightly stronger bond than the CoC , as suggested by the CCSDTQ/CBS results and the experimental D_0 values.

According to Eq. (4) and using the known $\text{IE}(\text{CoC}) = 7.73467 \pm 0.00007$ eV and $\text{IE}(\text{Co}) = 7.8810 \pm 0.00012$ eV,⁴⁴ we obtain $D_0(\text{Co}^+-\text{C}) - D_0(\text{Co-C}) = 0.14630 \pm 0.00014$ eV. Our CCSDTQ/CBS prediction of 0.175 eV for $D_0(\text{Co}^+-\text{C}) - D_0(\text{Co-C})$ is found to be higher than the experimental value by 29 meV. This deviation is mainly due to the overestimation (34 meV) of $\text{IE}(\text{Co})$ value by the CCSDTQ/CBS method. Similar overestimation of $\text{IE}(\text{Co})$ by coupled cluster theory has also been reported by Balabanov and Peterson.⁴⁷

D. Heats of formation for CoC and CoC^+

Applying the CCSDTQ/CBS procedure, the individual energy contributions to the atomization energies and $\Delta H^\circ_{f0}/\Delta H^\circ_{f298}$ values for CoC and CoC^+ are given in Table III. The experimental ΔH°_f 's of CoC and CoC^+ are not known. In view of the excellent agreement between our theoretical predictions and experimental measurements on the $\text{IE}(\text{CoC})$, $D_0(\text{Co-C})$, and $D_0(\text{Co}^+-\text{C})$, the CCSDTQ/CBS

values for $\Delta H^\circ_{f0}(\Delta H^\circ_{f298})$ of 775.7(779.2)/1522.5(1526.0) kJ/mol for CoC/CoC^+ predicted at the CCSDTQ/CBS level should be a reliable set of thermochemical data.

There appears to be an excellent agreement between the highly precise measurements obtained in the PFI-PE experiments²⁵ with the CCSDTQ/CBS results for the IE and D_0 of CoC/CoC^+ . Together with the previous works on FeC/FeC^+ and NiC/NiC^+ ,^{22,24} we conclude that the single-reference based coupled cluster approach is capable of predicting accurate thermochemical data with an uncertainty of ± 40 meV for the transition metal diatomics bearing considerable multi-reference character. As the CCSDTQ/CBS procedure includes the higher-order corrections for full triple and quadruple excitations in the coupled-cluster theory, these corrections seem to introduce some multi-reference remedy into the theoretical model.

IV. CONCLUSIONS

We have performed high-level *ab initio* calculations for the spectroscopic and energetic properties of CoC/CoC^+ at the coupled cluster and multi-reference configuration interaction levels using correlation consistent basis sets. The coupled cluster based CCSDTQ/CBS method involves the approximation to the CBS limit at the coupled cluster level up to full quadruple excitations along with ZPVE, CV (up to CCSDT level), SO coupling, SR, and HOC corrections (up to CCSDTQ level). The current theoretical calculations give the correct ground state of $^1\Sigma^+$ for CoC^+ . The CCSDTQ/CBS $\text{IE}(\text{CoC})$ of 7.740 eV is found to be 6 meV above the highly precise experimental IE value of 7.73467 ± 0.00007 eV determined by the two-color laser photoionization and photoelectron study of CoC^+ . Our theoretical results strongly suggest that the nominal single-reference based coupled cluster theory is capable of providing reliable IE prediction for CoC , despite the carbide's multi-reference character. On the other hand, the predicted ω_e (ω_e^+) of $\text{CoC}(\text{CoC}^+)$ values at the CCSD(T)/aug-cc-pV5Z level are significantly larger than the experimental data by 387 (112) cm^{-1} . It is found that the CCSDT and CCSDTQ methods can give more reliable predictions for ω_e (ω_e^+), with the CCSDTQ values of ω_e (ω_e^+) = 956 (992) cm^{-1} and r_e (r_e^+) = 1.560 (1.528) Å being in excellent agreement with experimental data of ω_e (ω_e^+) = 955 (985.6) cm^{-1} and r_e (r_e^+) = 1.561 (1.534) Å. The CCSDTQ/CBS $D_0(\text{Co}^+-\text{C})$ and $D_0(\text{Co-C})$ give the prediction of $D_0(\text{Co}^+-\text{C}) - D_0(\text{Co-C}) = 0.175$ eV, which is consistent with the experimental determination of 0.14630 ± 0.00014 eV. The current $D_0(\text{Co-C})$ and $D_0(\text{Co}^+-\text{C})$ predictions also favor the $D_0(\text{Co}^+-\text{C})$ value of 3.90 ± 0.30 eV by Hettich and Freiser,⁴⁵ which leads to the deduced value of $D_0(\text{Co-C}) = 3.75 \pm 0.30$ eV. The present calculations also provide the $\Delta H^\circ_{f0}(\Delta H^\circ_{f298})$ predictions for CoC/CoC^+ . An analysis of the correction terms in these calculations reveals that the core-valence and valence-valence electron correlations beyond CCSD(T) level and the relativistic effects indeed make significant contributions to the calculated thermochemical properties of CoC/CoC^+ . For the ΔH°_{f0} values of CoC/CoC^+ , we recommend the CCSDTQ/CBS predictions (in kJ/mol): $\Delta H^\circ_{f0}(\text{CoC}) = 775.7$ and $\Delta H^\circ_{f0}(\text{CoC}^+) =$

TABLE III. Individual energy contributions to the CCSDTQ/CBS atomization energies and $\Delta H^\circ_{f0}/\Delta H^\circ_{f298}$ values for CoC and CoC^+ .^a

		CoC	CoC ⁺
$\Delta E_{\text{extrapolated CBS}}^b$	wTQ5	369.9	-361.9
	wCQ5	372.6	-359.4
	Average	371.2	-360.6
ΔE_{CV}^c	(T) \rightarrow T	-1.4	0.4
ΔE_{ZPVE}^d		-5.9	-6.1
ΔE_{SO}^e		-8.7	-8.7
ΔE_{SR}^f	CCSD(T)	-13.3	-28.3
	(T) \rightarrow T	-0.8	0.1
	T \rightarrow Q	0.7	0.5
	Subtotal	-13.4	-27.7
ΔE_{HOC}^g	(T) \rightarrow T	-18.0	-13.6
	T \rightarrow Q	36.8	30.0
	Subtotal	18.8	16.4
CCSDTQ/CBS $\sum D_0^h$		360.6	-386.3
CCSDTQ/CBS $\Delta H^\circ_{f0}^i$		775.7	1522.5
CCSDTQ/CBS $\Delta H^\circ_{f298}^j$		779.2	1526.0

^aAll quantities and energy differences are in kJ/mol.

^bExtrapolated 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.

^cCore-valence electronic correlation obtained as the energy difference between CCSD(T) and CCSDT levels using the aug-cc-pwCVTZ basis set.

^dBased on the harmonic vibrational frequencies at the CCSDTQ/cc-pVTZ level.

^eSpin-orbit coupling obtained at the MRCl level with the uncontracted cc-pVTZ basis set.

^fScalar relativistic effect calculated at the CCSD(T)/aug-cc-pV5Z-DK, CCSDT/aug-cc-pVQZ-DK, and CCSDTQ/cc-pVTZ-DK levels.

^gHigher-order effect calculated at the CCSDT/aug-cc-pVQZ and CCSDTQ/cc-pVTZ levels.

^h $\sum D_0 = \Delta E_{\text{extrapolated CBS}} + \Delta E_{\text{CV}} + \Delta E_{\text{ZPVE}} + \Delta E_{\text{SO}} + \Delta E_{\text{SR}} + \Delta E_{\text{HOC}}$.

ⁱ $\Delta H^\circ_{f0} = \Delta H^\circ_{f0}(\text{C}) + \Delta H^\circ_{f0}(\text{Ni}) - \sum D_0$.

^j $\Delta H^\circ_{f298} = \Delta H^\circ_{f298}(\text{C}) + \Delta H^\circ_{f298}(\text{Ni}) - \sum D_0 - \text{thermal and enthalpy corrections}$.

= 1522.5, $\Delta H^{\circ}_{f298}(\text{CoC}) = 779.2$ and $\Delta H^{\circ}_{298}(\text{CoC}^+) = 1526.0$. These computed values should constitute a reliable set of thermochemical data for CoC/CoC⁺, which have not been measured experimentally.

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