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The standard enthalpy of formation of CH_2

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High-quality *ab initio* quantum chemical methods, including higher-order coupled cluster and full configuration interaction benchmarks, with basis sets ranging from [C/H] $[4s3p1d/2s1p]$ to $[9s8p7d5f4g3h2i/7s6p5d4f3g2h]$ have been employed to obtain the best technically possible value for the standard enthalpy of formation of $\tilde{X}\,^3B_1$ CH_2 and $\tilde{a}\,^1A_1$ CH_2. Careful extrapolations of finite basis MP2, CCSD, CCSD(T), and CCSDT energies to the complete basis set full configuration interaction limit plus inclusion of small corrections owing to relativistic effects, core correlation, and the diagonal Born–Oppenheimer correction results in the final extrapolated enthalpies of formation of this study, $\Delta_f H_0^{\rm o}(\tilde{X}\,^3B_1\ {\rm CH_2}) = 390.45^{+0.68}_{-0.64}\ {\rm kJ\,mol^{-1}}$ and $\Delta_f H_0^{\rm o}(\tilde{a}\,^1A_1\ {\rm CH_2}) = 428.10^{+0.68}_{-0.64}\ {\rm kJ\,mol^{-1}}$. The computed value for $\tilde{X}\,^3B_1$ CH_2 is in between the best two experimental results of 389.87 ± 0.86 and $390.73 \pm 0.66\ {\rm kJ\,mol^{-1}}$. The elaborate calculations leading to these enthalpies of formation also resulted in accurate estimates of the singlet-triplet splitting, $T_0(\tilde{a}\,^1A_1\ {\rm CH_2}) = 37.54^{+0.41}_{-0.29}\ {\rm kJ\,mol^{-1}}$, in excellent agreement with the best empirical value of $37.65 \pm 0.06\ {\rm kJ\,mol^{-1}}$, of the total atomization enthalpy, $D_0(\tilde{X}\,^3B_1\ {\rm CH_2}) = 753.03^{+0.43}_{-0.62}\ {\rm kJ\,mol^{-1}}$, in excellent agreement with the best experimental value of $753.3\ {\rm kJ\,mol^{-1}}$, of the bond dissociation energy, $D_{U1}^{\rm o}(0\ {\rm K})({\rm CH{-}H}) = 417.85 \pm 0.35\ {\rm kJ\,mol^{-1}}$, and of the quartic force field representations of the potentials of the two states around their respective minima. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1573180]

I. INTRODUCTION

Reproduction of bulk experimental data by chemical kinetic simulations requires the utilization of accurate thermochemical data, including the temperature-dependent standard enthalpies of formation, $\Delta_f H_T^{\rm o}$. This is especially true when temperature changes significantly during the experiments, like in combustion systems.[1–7] In a recent sensitivity analysis of the Leeds Methane Combustion Model[8] Turányi and co-workers[9] observed that in lean and stoichiometric methane flames the simulation errors are determined mainly by uncertainties in the enthalpy of formation of the OH, CH_2, HCCO, CH_2OH, and CH_2HCO radicals.

The enthalpy of formation of the OH radical, based on a spectroscopic approach employing the dissociation energy of $OH(A\,^2\Sigma^+)$, has recently been reinvestigated experimentally by Ruscic and co-workers[10] and lowered, based on a positive ion cycle approach, by as much as $2\ {\rm kJ\,mol^{-1}}$ to $36.94 \pm 0.33\ {\rm kJ\,mol^{-1}}$. The revised experimental value is fully supported by high-level *ab initio* electronic structure calculations.[10–12] Recently the enthalpy of formation of $^2\Pi$ CH has been investigated *ab initio* by us,[13] with a recommended value of $\Delta_f H_0^{\rm o} = 592.47^{+0.47}_{-0.56}\ {\rm kJ\,mol^{-1}}$. Here we extend this work and apply our computational procedure[13–17] to the CH_2 radical.

The various compilations of standard enthalpies of formation contain a large number of molecular systems whose data is very limited, scattered, and at times, contradictory.[18–27] Large uncertainties are found for both simple and complex molecular systems, and they are most prevalent for open-shell systems. Therefore, in order to improve upon currently available combustion models it is of utmost importance to obtain accurate enthalpies of formation with dependable error bars. With rapid advances in computing power and increasing sophistication in computational algorithms, first-principles (*ab initio*) approaches are likely to become the *de facto* standard for the determination of thermochemical properties for small and medium sized systems.[11–13,28–34] Assessment of the ultimate accuracy of the available *ab initio* approaches needs to be determined first for small systems, like the prototypical molecular systems OH,[10–12] CH,[13] SH,[17] and CH_2.

The empirical enthalpies of formation, $\Delta_f H_{298/0}^{\rm o}$, available for $^3CH_2$ ($\tilde{X}\,^3B_1$ CH_2) and $^1CH_2$ ($\tilde{a}\,^1A_1$ CH_2) from the literature[35–49] are summarized in Table I. The value of $\Delta_f H_0^{\rm o}(\tilde{X}\,^3B_1\ {\rm CH_2})$ has changed significantly over the years from $228\ {\rm kJ\,mol^{-1}}$ in 1954 (Ref. 35) to the currently accepted value of about $390\ {\rm kJ\,mol^{-1}}$, while

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TABLE I. Brief history of the empirical determination of the standard enthalpy of formation ($\Delta_f H_0^o$/kJ mol^{-1}) of $\tilde{X}\,^3B_1$ and $\tilde{a}\,^1A_1$ CH_2.[a]

Year	$\tilde{X}\,^3B_1$ CH_2	$\tilde{a}\,^1A_1$ CH_2	Ref.	Comment
1954	227.8		35	Electron-impact appearance potential of CH_2^+ ion from CH_3
1963	363.2±25.1		36	Study of disproportionation reaction 2 $CH_2 \rightarrow CH + CH_3$
1963	328.0±25.1		36	Chemical equilibrium involving CH_2 at high temperatures
1964	355.6		37	Review
1965	<392.9±2.9		38	Appearance potential of CH_2^+ from CH_4
1966	376.6±16.7		39	Review of kinetic data
1968	384.5±4.2		40	Heat of formation of CH_3 and ionization potential of CH_2
1968	<395.8		41	
1969	418.4±41.8		42	Electron impact measurements
1969	<399.6		43	
1976	392.5±2.1		44	Photoionization of CH_4
	390.8±1.7		44	Photoionization of ketene
1978		425.5±2.1	45	Photolysis of ketene
1982	393.7±2.5	429.3±2.5	47	Molecular beam photodissociation of CH_4
1985	388.3±2.5	425.9±2.1	46	Photodissociation of ketene
1997	389±4		24	JPL review
1999	390.45±4.02		25	NIST review
1999	389.87±0.84		48	Solution of local thermochemical network
2000	390.45±4.02	428.27±4.02	26	
2001	390.45±4.02	428.36±4.02	27	CRC Handbook
2002	390.73±0.66	428.36±4.02	49	Appearance ionization energy of CH_2^+

[a] When only $\Delta_f H_{298}^o$ was given in the literature, the value was converted to $\Delta_f H_0^o$ using a correction of −0.42 kJ mol^{-1} (see text).

$\Delta_f H_0^o(\tilde{a}\,^1A_1\ CH_2)$ has ranged from 425 kJ mol^{-1} to 429 kJ mol^{-1}. The smaller spread for $\tilde{a}\,^1A_1$ CH_2 is due to the lack of early data on the enthalpy of formation of $^1CH_2$. The converged values presented in standard recent compilations[19,20,24–27] have a substantial uncertainty of 4 kJ mol^{-1}. A considerably tighter estimation of $\Delta_f H_{298/0}^o$ can be expected from state-of-the-art *ab initio* procedures.[13,17] The mean values of the two most recent experimental/empirical estimates for $\Delta_f H_0^o(\tilde{X}\,^3B_1\ CH_2)$, 389.87±0.86 kJ mol^{-1},[48] based on the simultaneous solution of a local thermochemical network, and 390.73 ±0.66 kJ mol^{-1},[49] based on a new high-quality estimate of the ionization energy of CH_2, still differ by almost 1 kJ mol^{-1}.

In modern molecular electronic structure theory the two most significant sources of computational error in energies and properties are due to the truncation of the atomic orbital (AO) basis set (one-electron space) and the truncation of the n-electron space of all Slater determinants that constitute the full configuration interaction (FCI) wave function. To obtain the best technically possible results, both the one- and n-particle limits must be advanced. These limits define the focal point of all systematic electronic structure calculations attempting to get definitive energy and property predictions.[14,15,50] A particularly attractive technique for the calculation of accurate energetics with well-established error estimates is the focal-point technique.[14,15] Extrapolation to both the one- and n-particle limits is part of this scheme, as well as computation of (small) auxiliary terms readily neglected in most theoretical treatments, namely, effects owing to core correlation,[51,52] special relativity,[53–55] and the diagonal Born–Oppenheimer correction (DBOC).[56–58] The methods defined as model chemistries including Gaussian-X,[59–64] CBS,[65,66] and W-X (Refs. 11, 32) may be considered as approximations to the focal-point scheme. In this study the focal-point scheme is employed to compute the standard enthalpies of formation of $\tilde{X}\,^3B_1$ CH_2 and $\tilde{a}\,^1A_1$ CH_2. Accurate and purely *ab initio* computation of (temperature-dependent) standard enthalpies of formation require several types of energetic information, most importantly atomization energies, bond dissociation energies, and zero-point energies. Investigation of these quantities forms part of our present investigation of $\Delta_f H_{298/0}^o(CH_2)$.

II. ELECTRONIC STRUCTURE CALCULATIONS

The focal-point scheme employed throughout this study requires the use of convergent one-particle basis sets and electronic structure methods. The correlation-consistent (cc) family of basis sets (aug)-cc-p(C)VXZ [with cardinal number $X=2$(D), 3(T), 4(Q), 5, and 6],[67–70] which systematically approach the complete basis set (CBS) limit, were therefore employed in the focal-point basis set extrapolations. Specifically, the formulas $E^X = E_{CBS} + a\exp(-bX)$ and $E^X = E_{CBS} + cX^{-3}$ were used for estimating the Hartree–Fock[71] correlation energy limits,[15,33,50] respectively. In accordance with the usual focal-point notation, the δ[CCSD] and δ[CCSD(T)] correlation energy increments, employed extensively in the tables, are defined as the electronic energy difference with respect to the next lowest level of theory. In the CBS results of the tables the cardinal numbers of the basis sets empoyed for extrapolation are indicated in parentheses, e.g., CBS(a56), where a stands for augmentation (aug).

The electronic structure of $\tilde{X}\,^3B_1$ CH_2 is dominated by a single configuration, $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^1(1b_1)^1$, and is therefore accurately described by single-reference (SR) electronic structure techniques. However, $\tilde{a}\,^1A_1$ CH_2 has diradical character and the electronic configurations $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2$ and $(1a_1)^2(2a_1)^2(1b_2)^2(1b_1)^2$ are both important reference configurations. This results in the SR methods providing an unbalanced description because $\tilde{X}\,^3B_1$ CH_2 is treated more accurately than $\tilde{a}\,^1A_1$ CH_2. Fortunately, this imbalance is much reduced as higher excitation levels are included in the electronic structure computation. This requirement is satisfied by the high-level configuration interaction and coupled cluster wave functions employed in the current study.

Reference electronic wave functions have been determined by the single-configuration restricted (open-shell) Hartree–Fock [R(O)HF] method. Dynamical electron correlation was accounted for by the coupled cluster (CC) method including all double (CCSD) (Ref. 72) and triple (CCSDT) (Refs. 73–75) excitations. The effects of connected triple excitations were also accounted for perturbatively through the CCSD(T) method.[76,77] The configuration interaction (CI) computations [CISD(CI2), CISDT(CI3), CISDTQ(CI4), CISDTQP(CI5), and CISDTQPH(CI6)] were expanded to the full configuration interaction (FCI) limit[78] with smaller basis sets. For valence correlation energy computations the 1*s* core orbital of carbon was excluded, while virtual orbitals were never deleted from the active space.

Recently we suggested[16] a simple multiplicative procedure, termed scaled higher-order correlation or SHOC, to estimate higher-order correlation (HOC) effects. This scheme seems to be sucessful when used to correct the energies obtained in CCSD(T) or CCSDT computations.[13,16,17] The SHOC procedure utilizes the observation that HOC energies show limited basis set dependence and thus even at the CBS limit they can be estimated from explicit small basis set FCI and CCSD(T) or CCSDT calculations.

Optimum geometries for $\tilde{X}\,^3B_1$ and $\tilde{X}\,^1A_1$ CH_2 were obtained with analytic gradients at the all-electron aug-cc-pCVQZ R(O)HF-CCSD(T) level of theory. Therefore, results of our optimizations reflect the substantial bond length reduction[52] due to the inclusion of core-valence correlation. The resulting $[r_e(\mathrm{CH}), \angle_e(\mathrm{HCH})]$ structural parameters are [1.075 981 Å, 133.8483°] and [1.106 907 Å, 102.1369°] for $^3CH_2$ and $^1CH_2$, respectively. These geometries were adopted for all subsequent computations involved in the focal-point analysis including the auxiliary DBOC, relativistic, and core-valence correlation corrections, and in the determination of the quartic force field. Comparison between the best available empirical and the present computational estimates of the r_e structures of $^3CH_2$ and $^1CH_2$ show an almost perfect agreement for both states. To wit, for $^3CH_2$ the best empirical estimates are $r_e(\mathrm{CH}) = 1.0753(3)$ Å and $\angle_e(\mathrm{HCH}) = 133.93(1)°$, while for $^1CH_2$ they are $r_e(\mathrm{CH}) = 1.1066(3)$ Å and $\angle_e(\mathrm{HCH}) = 102.37°$.[79]

Core correlation effects were determined from all-electron and frozen-core treatments up to CCSDT with the aug-cc-pCV*XZ* ($X = 2$, 3, 4, and 5) basis sets, while FCI calculations were performed with the aug-cc-pCVDZ basis set. Relativistic effects were gauged by first-order perturbation theory applied to the one-electron mass-velocity and Darwin terms (MVD1).[53–55] Computation of the DBOC correction[56,57] was performed at the Hartree–Fock level within the formalism of Handy, Yamaguchi, and Schaefer[56] using the BORN program operating within the PSI package.[80] Different versions of the program packages ACES II,[81,82] PSI,[80,83] and DIRCCR12-95,[84,85] were utilized for the electronic structure computations.

Tables containing the raw energetic data used for the focal-point analysis are provided as supplementary material.[86]

III. ZERO-POINT VIBRATIONAL ENERGIES

Ab initio anharmonic (quartic) force fields[87] can provide an accurate assessment of zero-point energies (ZPEs) for semirigid molecular species, as long as the equilibrium structures are contained in a deep well.[88,89] The full quartic force fields of $\tilde{X}\,^3B_1$ CH_2 and $\tilde{a}\,^1A_1$ CH_2 were computed at the same level of theory as the equilibrium geometries reported above, all-electron aug-cc-pCVQZ CCSD(T), thus eliminating the nonzero force dilemma.[90] The derivatives through quartic terms were determined,[87] using the MATHEMATICA program package,[91] from finite difference formulas of analytic first derivatives computed at displaced equilibrium geometries of $\Delta r = \pm 0.01$, ± 0.02 Å, $\Delta\angle\mathrm{HCH} = \pm 0.01$, ± 0.02 rad, and their appropriate combinations. The internal coordinate representation of the quartic force field, reported in Table II, was analytically transformed to Cartesian coor-

TABLE II. Theoretical [aug-cc-pCVQZ R(O)CCSD(T)] quartic force fields of the $\tilde{X}\,^3B_1$ and $\tilde{a}\,^1A_1$ electronic states of CH_2.[a]

Constant	$\tilde{X}\,^3B_1$		$\tilde{a}\,^1A_1$
	This work	Ref. 95	This work
RR	5.8403	5.7707(72)	4.8357
RR'	−0.0880	−0.0950(19)	−0.0302
$R\alpha$	0.1099	0.1513(21)	0.2214
$\alpha\alpha$	0.3627	0.3665(28)	0.6678
RRR	−33.704	−34.86(19)	−28.355
RRR'	0.0213		−0.0384
$RR\alpha$	0.0572		−0.0129
$RR'\alpha$	−0.1513	−0.112(11)	−0.3704
$R\alpha\alpha$	−0.0619	[−0.1888]	−0.1798
$\alpha\alpha\alpha$	−0.7465		−0.6273
$RRRR$	172.87	154.7(32)	145.83
$RRRR'$	−0.488		−0.581
$RRR'R'$	−0.407		0.082
$RRR\alpha$	−0.653		−1.200
$RRR'\alpha$	0.041		−0.015
$RR\alpha\alpha$	−0.068		−0.339
$RR'\alpha\alpha$	0.259	0.140	0.436
$R\alpha\alpha\alpha$	0.232		0.537
$\alpha\alpha\alpha\alpha$	−0.884		−0.600

[a] Reference geometries, (R/Å, $\angle\mathrm{HCH} = \alpha$/deg), of $\tilde{X}\,^3B_1$ and $\tilde{a}\,^1A_1$ CH_2 are (1.075 981, 133.8483) and (1.106 907, 102.1369), respectively. The internal coordinates (R, R', α) employed correspond to the choice (bond length, bond length, bond angle). All force constants correspond to energy measured in aJ, bond distance in Å, and bond angle in radians. The values in parentheses refer to one standard deviation. The values in brackets refer to constrained values.

TABLE III. Theoretical and experimental harmonic frequencies (ω_i), anharmonic constants (χ_{ij}), and fundamental vibrational frequencies (ν_i) of $\tilde{X}\,^3B_1$ and $\tilde{a}\,^1A_1$ CH_2.[a]

	$\tilde{X}\,^3B_1$			$\tilde{a}\,^1A_1$		
	This work	TZP CISD[b]	Expt.[c]	This work	TZP CISD[b]	Expt.[d]
ω_1	3148.0	3178.7		2929.3	2954.5	
ω_2	1091.2	1147.6		1400.1	1420.1	
$\omega_3(b_2)$	3376.9	3404.5		3004.6	3022.4	
χ_{11}	−29.45(−29.55)	−28.3		−31.79(−32.13)		
χ_{12}	(0.33)	0.5		(6.73)		
χ_{13}	−113.33(−114.68)	−110.4		−121.57(−124.96)		
χ_{22}	(−40.98)	−33.4		(−17.18)		
χ_{23}	(2.32)	−0.5		(−14.70)		
χ_{33}	−33.81(−36.66)	−35.2		−31.79(−37.47)		
ν_1	3035.6(3031.7)	3067.1		2804.5(2806.0)		2806.0
ν_2	964.6(1010.6)	1080.7	963.1	1358.2(1361.8)		1352.6
$\nu_3(b_2)$	3248.9(3247.3)	3278.7		2860.4(2859.8)		2865.0
Δ_1	−116.3	−111.6		−123.37		
Δ_2	−80.6	−66.9		−38.33		
Δ_3	−129.5	−125.8		−144.78		
ZPE(harm)	3808.0	3865.4		3667.0	3698.5	
ZPE(VPT2)	3736.4(3753.2)	3813.6		3612.0(3612.1)		

[a] See footnote a in Table II. All entries are given in cm^{-1}. The molecular constants reported refer to all-electron aug-cc-pCVQZ ROCCSD(T) electronic wave functions. Δ_i stands for $\nu_i - \omega_i$. The spectroscopic constants under the heading "This work" were obtained by the NRLH approach, and the corresponding values in parentheses were obtained by VPT2.
[b] Reference 88.
[c] Reference 119.
[d] Reference 101.

dinate space using INTDER95.[90,92] Various spectroscopic constants,[88,93] determined from the quartic force fields in normal coordinate space, are given in Table III along with selected theoretical and experimental values.

The literature contains a vast amount of data on the ZPEs of $\tilde{X}\,^3B_1$ CH_2 and $\tilde{a}\,^1A_1$ CH_2. In the brief summary below, we employ the notation of ^{1}ZPE and ^{3}ZPE for the ZPEs of $\tilde{a}\,^1A_1$ CH_2 and $\tilde{X}\,^3B_1$ CH_2, respectively, while ΔZPE refers to the ZPE difference between the singlet and triplet states ($^1\mathrm{ZPE}-{}^3\mathrm{ZPE}$). Unlike in other parts of this paper, energy values of this and the next section are given in cm^{-1}.

In 1983 McKellar and co-workers,[94] using the crude approximation that the stretching ZPEs are similar for the two states, determined the ZPE for the bending modes of the triplet and singlet states as 670 and 499 cm^{-1}, respectively, leading to a ΔZPE of -171 cm^{-1}. Two years later, Leopold and co-workers[46] obtained a ΔZPE estimate of $+100 \pm 140$ cm^{-1} from the deuterium shifts of photoelectron spectra of CH_2^- and CD_2^-, and consequently derived a ^{3}ZPE of 3430 ± 140 cm^{-1} and a ^{1}ZPE of 3530 cm^{-1}. In a subsequent study McLean and co-workers,[95] using SOCI+Q energy points and a variational nonrigid bender Hamiltonian approach, obtained 3710 ± 20 cm^{-1} for ^{3}ZPE. A value for ^{1}ZPE of 3620 ± 20 cm^{-1} was determined by them from a fit to the available experimental data. In 1989 Comeau and co-workers,[96] based on $[5s4p3d2f1g/3s2p1d]$ MR-CISD +Q PESs and the Morse oscillator rigid bender internal dynamic (MORBID) Hamiltonian approach, determined a ΔZPE of -125 cm^{-1}, with ^{1}ZPE and ^{3}ZPE values of 3586 and 3711 cm^{-1}, respectively. In a subsequent study, based on small adjustments to the *ab initio* potential of Comeau and co-workers[96] in order to better reproduce the available rovibrational levels, Jensen and Bunker,[97] again using their MORBID approach for solution of the nuclear motion problem, obtained 3689 cm^{-1} for ^{3}ZPE and 3613 cm^{-1} for ^{1}ZPE, resulting in a ΔZPE of -76 cm^{-1}. For a long time these values remained the best empirical estimates for these quantities. In a recent publication Gu and co-workers[98] investigated the effect of the Renner–Teller interaction of the $\tilde{a}\,^1A_1$ state with the $\tilde{b}\,^1B_1$ state and found that the adiabatic zero-point energy of $\tilde{a}\,^1A_1$ CH_2 changes substantially, to 3621 cm^{-1}, by inclusion of a rotational contribution.[99] Therefore, the latest estimate for ΔZPE from Jensen and Bunker, including the Renner–Teller interaction of the $\tilde{a}$ and $\tilde{b}$ electronic states, is $3621-3689=-68$ cm^{-1}.

The present quartic force field representations of the PESs of the $\tilde{X}\,^3B_1$ and $\tilde{a}\,^1A_1$ electronic states of CH_2 allow for three different estimates of the ZPEs. The first, and simplest, approach is afforded by the harmonic frequencies computed from the quadratic parts of the force fields, yielding values of 3808 cm^{-1} (^{3}ZPE), 3667 cm^{-1} (^{1}ZPE), and -141 cm^{-1} (ΔZPE). The second, more sophisticated, method uses relations derived from second-order vibrational perturbation theory (VPT2),[88,93] in order to yield ZPE(VPT2), after utilization of the full quartic force fields (Table III). This treatment yields 3753, 3612, and -141 cm^{-1} for ^{3}ZPE(VPT2), ^{1}ZPE(VPT2), and ΔZPE(VPT2), respectively. Therefore, inclusion of vibrational anharmonicity through VPT2 does not change ΔZPE. However, there are problems with describing the ZPEs of either $\tilde{X}\,^3B_1$ CH_2 or $\tilde{a}\,^1A_1$ CH_2 with VPT2. VPT2 is only valid as long as each internal coordinate being described is contained in a deep well. The

PES of $\tilde{X}\,^3B_1$ CH_2 is rather shallow along the bending mode, with the barrier to linearity being less than 2000 cm^{-1} and a bending frequency of about 1000 cm^{-1}. This evidence along with the large equilibrium bond angle suggests that $\tilde{X}\,^3B_1$ CH_2 is almost quasilinear.[100] Thus, for this state simple VPT2 offers a somewhat unreliable approach. This observation should be at least partially responsible for the larger than usual (47 cm^{-1}) overestimation of the experimentally observed ν_2 value. For $\tilde{a}\,^1A_1$ CH_2, the Renner–Teller interaction with $\tilde{b}\,^1B_1$ CH_2 has been shown[98] to have a (small) effect on the ZPE, rendering the VPT2 approach, without considering any rotational effects, somewhat suspect. On the other hand, the CCSD(T) technique overcomes the difficulty of a single-reference-based description of $\tilde{a}\,^1A_1$ CH_2, as seen from the excellent agreement between the computed and experimental[101] vibrational fundamentals. This excellent agreement ensures that the effective adiabatic vibrational zero-point energy of $\tilde{a}\,^1A_1$ CH_2 should indeed be very close to 3612 cm^{-1}, our computed value, which is a value in fact only 1 cm^{-1} away from the MORBID result of Jensen and Bunker[97] and only 9 cm^{-1} away from the latest result of Gu *et al.*[98]

The third, most sophisticated approach to calculate ZPEs from the force field representations of the potentials employs the so-called nonrigid-rotation-large-amplitude-internal-motion Hamiltonian (NRLH) method of Szalay.[102–104] The NRLH method amounts to an adiabatic separation of the bending and stretching motions. The bending motion is described by a geometrically defined curvilinear coordinate, while rectilinear displacement coordinates describe the stretching motions. The effect of stretching vibrations on the bending motion is taken into account by second-order perturbation theory. This approach, utilizing again the full quartic force fields of Table III, yields 3736, 3612, and -124 cm^{-1} for ^{3}ZPE, ^{1}ZPE, and ΔZPE, respectively. It is remarkable how close the computed VPT2 and NRLH anharmonic frequencies are for $\tilde{a}\,^1A_1$ CH_2, which exhibits a small-amplitude bending motion, and how much better the NRLH bending frequency is for the ground state, where the deviation between experiment and theory decreases from 47.5 (VPT2) to 1.5 (NRLH) cm^{-1}.

In summary, it seems that for the quantities of most interest for the present study, ^{3}ZPE, ^{1}ZPE, and ΔZPE, the best overall theoretical estimates of this study, which will be used exclusively in what follows, are 3736^{+15}_{-15}, 3612^{+10}_{-10}, and -124^{+18}_{-18} cm^{-1}, respectively. The relatively small error bars of these values reflect our confidence in the computed values, although the ^{3}ZPE and ΔZPE values are substantially different from the values recommended by Gu *et al.*[98] Further studies are needed to explain this discrepancy.

IV. SINGLET–TRIPLET ENERGY SPLITTING

To check for the accuracy of the focal-point approach[14,15] for the present system, we decided to undertake a comprehensive computational investigation of the singlet–triplet splitting, $T_e(\tilde{a}\,^1A_1)$. The *ab initio* results obtained as part of this study are reported in Tables IV and V. These results complement the experimental/empirical and the plethora of theoretical data available on the singlet–triplet splitting energy of CH_2.[45–47,94–97,105–109] A comprehensive review,[108] containing results up to 1997, on the singlet–triplet splitting in CH_2 has been presented. In the following year, Sherrill, Leininger, and co-workers[109] extended these results by adding TZ2P FCI numbers to the compendium of theoretical results. Readers interested in the history of the empirical and theoretical determination of the singlet–triplet splitting energy are referred to these and the original publications.

A. Valence-only results

Two series for the valence-only focal-point results for the singlet-triplet energy splitting have been generated (see Table IV). Series CC corresponds to coupled-cluster (CC) theory, while series CI involves results obtained with configuration interaction (CI) techniques up to FCI. The data obtained reveal the following about the S–T energy splitting of CH_2, $T_e(\tilde{a}\,^1A_1)$, and its *ab initio* determination:

(1) Extension of the one-particle basis set coupled with the use of convergent electron correlation treatments systematically lowers the S–T separation energy.

(2) Augmenting the one-particle basis set with diffuse functions improves the description of S–T splitting, such that the aug-cc-pV*XZ* and cc-pV$(X+1)$Z results are of comparable accuracy.

(3) The Hartree–Fock contribution to the S–T energy splitting is fairly basis set independent, changing by only 224 cm^{-1} from 8850 cm^{-1} (cc-pVDZ) to 8626 cm^{-1} (CBS limit). The imbalanced treatment of $\tilde{a}\,^1A_1$ CH_2 is corrected by the inclusion of double substitutions into the electronic wave function. The resulting changes to $T_e(\tilde{a}\,^1A_1)$, at the CBS limit, are substantial at -3962 (MP2), -4176 (CISD), and -5099 (CCSD) cm^{-1}, respectively. Significant contributations are also found for the (T) correction to CCSD, -322 cm^{-1}, and for the effect of triples and quadruple substitutions on CI, -1141 cm^{-1} (CISDTQ). The last corrections reflect that the truncated CI expansions are more dependent on the reference wave function than the CC expansions.

(4) The higher-order electron correlation contributions, beyond those included in CCSD(T) or CISDTQ, are relatively insensitive to the basis set, thus making the accurate *ab initio* calculation of $T_e(\tilde{a}\,^1A_1)$ possible.

(5) The generated FCI data facilitate the determination of scaled higher-order correlation (SHOC) factors for both electronic states of interest. The SHOC factor is computed as the ratio of the FCI correlation energy and the correlation energy of a truncated method. The SHOC factors have limited basis set dependence,[13,16] and therefore may be used to estimate the FCI limit. For example, the SHOC factors for the CCSDT method in a cc-pVTZ basis are 1.000 459 and 1.001 327 for the $\tilde{X}$ and $\tilde{a}$ states, respectively. It should be noted that the CCSD(T) SHOC factors are considerably larger at 1.003 738 ($\tilde{X}$) and 1.006 143 ($\tilde{a}$). In this study, the cc-pVTZ SHOC factors

TABLE IV. Valence focal-point analysis of the energy difference (singlet–triplet splitting, in cm^{-1}) between the corresponding minima of the $\tilde{X}\,^3B_1$ and $\tilde{a}\,^1A_1$ electronic states of CH_2.[a]

Series CC	ΔE_e(HF)	δ[CCSD]	δ[CCSD(T)]	δ[CCSDT]	δ[SHOC]	ΔE_e(CC)
cc-pVDZ (24)	8850	−1626	−248	−76	−28	4114
cc-pCVDZ (28)	8856	−1615	−249	−75		
cc-pV(T/D)Z (40)	8759	−1491	−288	−75		[3643]
aug-cc-pVDZ (41)	8452	−1511	−267	−71		[3604]
cc-pVTZ (58)	8736	−1445	−296	−74	−34	3499
cc-pCVTZ (71)	8734	−1432	−298	[−74]	[−34]	[3479]
aug-cc-pVTZ (92)	8604					
cc-pVQZ (115)	8666	−1314	−310	[−74]	[−34]	[3267]
cc-pCVQZ (144)	8663	−1305	−311			
aug-cc-pVQZ (172)	8621	−1265	−315			
cc-pV5Z (201)	8640	−1237	−316			
aug-cc-pV5Z (287)	8626	−1209	−319	[−74]	[−34]	[3150]
cc-pV6Z (322)	8629	−1199	−319	[−74]	[−34]	[3145]
aug-cc-pV6Z (443)	8626	−1179	−320	[−74]	[−34]	[3131]
CBS[b]	8626	−1137	−322	[−74]	[−34]	[3097]

Series CI[c]	ΔE_e(HF)	δ[CI2]	δ[CI3]	δ[CI4]	δ[CI5]	δ[FCI]	ΔE_e(CI)
cc-pVDZ (24)	8850	−3735	−105	−861	−22	−10	4117
cc-pV(T/D)Z (40)	8759	−4000	−126	−983	−30	−12	3608
aug-cc-pVDZ (41)	8452	−3815	−119	−908	−26	−10	3574
cc-pVTZ (58)	8736	−4053	−123	−1018	−31	−12	3499
aug-cc-pVTZ (92)	8604	−4106					
cc-pVQZ (115)	8666	−4176	[−123]	[−1018]	[−31]	[−12]	[3306]

[a] For each basis set the total number of contracted Gaussian functions is given in parentheses. For correlated-level calculations the symbol δ denotes the increment in the relative energy (ΔE_e) with respect to the preceding level of theory as given by the hierarchy RHF→MP2→CCSD→CCSD(T)→CCSDT→FullCC and RHF→CI2(CISD)→CI3(CISDT)→CI4(CISDTQ)→CI5(CISDTQP)→FullCI for Series CC and Series CI, respectively. Brackets signify assumed increments from smaller basis set results. The scaled higher-order correction (SHOC) multiplicative factor was computed as (1.000 459, 1.001 327) for ($^3CH_2$, $^1CH_2$) at the cc-pVTZ CCSDT level. All values are given in cm^{-1}.

[b] The complete basis set (CBS) RHF difference is obtained by extrapolation of aug-cc-pV(Q,5,6)Z energies. The CBS correlation increments are obtained by extrapolation of aug-cc-pV(5,6)Z results.

[c] The computed FCI energies have been determined employing 786 897 (cc-pVDZ), 20 899 977 [cc-pV(T/D)Z], 24 500 738 (aug-cc-pVDZ), and 214 268 028 (cc-pVTZ) determinants.

will be utilized to estimate the FCI limit for larger basis set CCSD(T) and CCSDT computations. The CCSDT scale factors provide estimates of the cc-pVDZ FCI $T_e(\tilde{a}\,^1A_1)$ to within 3 cm^{-1}.

(6) The valence-only CBS FCI $T_e(^1A_1)$ value is 3097^{+25}_{-5} cm^{-1}, where the conservative error estimate is based on the possible overestimation of the CCSD–HF energy increment due to the uncertainty of the extrapolations employed.

TABLE V. Core correlation corrections, in cm^{-1}, to the pure energy difference (singlet–triplet splitting) between the corresponding minima of the $\tilde{X}\,^3B_1$ and $\tilde{a}\,^1A_1$ electronic states of CH_2.[a]

Series CC	δ[MP2]	δ[CCSD]	δ[CCSD(T)]	δ[CCSDT]
cc-pCVDZ (28)	+5	+36	−17	−3
cc-pCVTZ (71)	+71	+54	−30	−9
cc-pCVQZ (144)	+110	+59	−35	
aug-cc-pCVQZ (201)	+110	+59	−35	
cc-pCV5Z (255)	+119	+59	−36	
aug-cc-pCV5Z (341)	+119	+59	−36	
aug-cc-pCV6Z (533)	+122	+59	−37	
CBS[a56][b]	+126	+58	−37	

[a] See footnote a in Table IV.

[b] The complete basis set (CBS) δ[MP2], δ[CCSD], and δ[CCSD(T)] values were obtained by a polynomial (X^{-3}) extrapolation of the best two (aug-cc-pCV5Z and aug-cc-pCV6Z) available values, resulting in the CBS[a56] estimates.

B. Effect of core correlation

High-accuracy *ab initio* computations of energy differences have shown[51,52,110] that a proper description of core-core and core-valence correlation is essential in order to approach the technical limits of nonrelativistic electronic structure theory. In this study the (aug)-cc-pCV*XZ* basis sets were employed in conjunction with MP2, CCSD, CCSD(T), and CCSDT electronic structure techniques. The computations, summarized in Table V, reveal that the core correlation is substantial at about +100 cm^{-1}. The positive value of the core correlation correction indicates that the triplet state is stabilized more than the singlet state. As observed previously for molecules containing first-row elements,[13,15] the core correlation correction computed at the MP2 level of theory accurately approximates the correction for higher-level methods, like CCSD(T) and CCSDT. Furthermore, although the cc-pCVDZ basis set provides a poor MP2 estimate of the core correlation energy (+5 cm^{-1} versus +126 cm^{-1} at the CBS limit), the incremental changes of higher-order methods are computed reasonably well, +36 cm^{-1} versus +59 cm^{-1} for CCSD and −17 cm^{-1} versus −37 cm^{-1} for CCSD(T).

TABLE VI. Valence focal-point analysis of the total atomization energy of $\tilde{X}\,^3B_1$ CH_2 in kJ mol^{-1}.[a]

Basis	HF	δ[CCSD]	δ[CCSD(T)]	δ[CCSDT]	δ[FCI]	FCI
cc-pVDZ(5/14)	631.27	+107.98	+2.10	+0.11	+0.18	741.64
cc-pVTZ(14/30)	645.47	+132.10	+3.54	−0.01	+0.14	781.24
cc-pVQZ(30/55)	647.03	+139.20	+3.90	−0.06	[+0.14]	[790.21]
cc-pV5Z(55/91)	647.49	+141.12	+4.03	[−0.06]	[+0.14]	[792.72]
cc-pV6Z(91/140)	647.55	+141.83	+4.00	[−0.06]	[+0.14]	[793.46]
CBS[456]	647.56	+142.81	[+4.00]	[−0.06]	[+0.14]	[794.45]
aug-cc-pVDZ(9/23)	632.99	+111.11	+2.53	+0.17	+0.16	746.96
aug-cc-pVTZ(23/46)	646.13	+134.28	+3.74	−0.06	[+0.16]	
aug-cc-pVQZ(46/80)	647.21	+139.98	+3.99	[−0.06]	[+0.16]	
aug-cc-pV5Z(80/127)	647.52	+141.44	+4.05	[−0.06]	[+0.16]	
aug-cc-pV6Z(127/189)	647.56	+142.03	+4.01	[−0.06]	[+0.16]	
CBS[456]	647.57	+143.34	+3.83	[−0.06]	[+0.16]	[794.84]

[a] After each basis set the number of contracted Gaussian basis functions for H/C is given in parentheses. See footnote a in Table IV for details.

Due to the opposite signs of δ[CCSD] and δ[CCSD(T)] increments, an accurate assessment of core correlation may be obtained by a large or complete basis set MP2 computation or extrapolation, appended with coupled cluster corrections obtained with any of the smaller basis sets. Our estimate of the core correlation correction includes the CBS(a56) CCSD(T) extrapolated value augmented with the cc-pCVQZ CCSDT incremental change, providing a dependable result of $139\pm5\ \mathrm{cm}^{-1}$, only $13\ \mathrm{cm}^{-1}$ higher than the CBS MP2 value.

C. Relativistic and adiabatic corrections

In approaching the one- and n-particle limits it becomes essential to include corrections typically neglected in nonrelativistic electronic structure calculations, such as the effects of special relativity and the adiabatic correction of the Born–Oppenheimer approximation.

Simple and efficient methods exist for computing relativistic corrections for molecules containing first-row elements, for a review see, e.g., Ref. 55. In the current study, the energy corrections due to the one-electron mass-velocity and Darwin terms (MVD1) have been computed with the ACESII program package[81] at the cc-pCV5Z CCSD(T) level of theory, resulting in a $21.5\ \mathrm{cm}^{-1}$ correction, with a correlation energy correction of $-2.0\ \mathrm{cm}^{-1}$. This correction preferentially stabilizes the singlet electronic state, and differs significantly from a previous estimate of $-14\ \mathrm{cm}^{-1}$, obtained with a medium-size basis set and ROHF and two-configuration SCF calculations for $^3CH_2$ and $^1CH_2$, respectively.[111] The MVD1 correction approximates the Dirac–Coulomb–Pauli Hamiltonian quite accurately for all molecules containing first-row elements only.[55,112] More sophisticated but still simple relativistic corrections would include the two-electron Darwin, the Breit, and the Lamb-shift effects.[113,114] Since these corrections are considered to be too small to be relevant for this study (usually[55] they are comparable to the correlation contribution to the MVD1 correction), they have not been computed. Therefore, our final estimate for the relativistic correction of the S–T energy splitting is $-22\pm5\ \mathrm{cm}^{-1}$.

The first-order, adiabatic correction to the Born–Oppenheimer approximation is the diagonal Born–Oppenheimer correction (DBOC). The landmark paper of Handy, Yamaguchi, and Schaefer[56] reported a substantial correction of $+38\ \mathrm{cm}^{-1}$, obtained at the DZP SCF level, stabilizing the triplet ground state. Although to achieve spectroscopic accuracy during prediction of rovibrational spectra the Hartree–Fock level may not be sufficiently accurate to obtain the adiabatic correction,[115] it appears to be sufficiently accurate for this study. Employing a larger TZ2P+f basis the DBOC correction increases to $+48\ \mathrm{cm}^{-1}$; therefore our best estimate is $48\pm15\ \mathrm{cm}^{-1}$.

D. Total singlet–triplet splitting

The converged *ab initio* data supply an accurate singlet–triplet energy splitting for CH_2. The current high-quality estimate of the singlet–triplet splitting, provided by the valence focal point method, augmented with corrections resulting from core correlation, relativity, and the diagonal Born–Oppenheimer correction is $3097^{+25}_{-5}+139^{+5}_{-5}-22^{+5}_{-5}+48^{+15}_{-15}$, yielding $T_e\ (\tilde{a}\,^1A_1)=3262^{+29}_{-16}\ \mathrm{cm}^{-1}$. The best empirical estimate of the singlet–triplet splitting of the minima of the relativistic adiabatic (effective) potentials is $3156-3621+3689=3224\ \mathrm{cm}^{-1}$.[116] The final correction to consider for our computed value is the ZPE difference between the singlet and triplet states. As discussed in Sec. III, we recommend the value of $-124^{+18}_{-18}\ \mathrm{cm}^{-1}$. This ΔZPE value brings our computed estimate, $3138^{+34}_{-24}\ \mathrm{cm}^{-1}$, in excellent accord with the best experimental result of $T_0\ (\tilde{a}\,^1A_1)=3147\pm5\ \mathrm{cm}^{-1}$.[97,98] The accuracy of the current computational study suggests that to decrease the error bar of the computed singlet–triplet splitting our estimate for the ZPE correction must be further investigated and its error bars tightened.

V. TOTAL ATOMIZATION ENERGY OF $\tilde{X}\,^3B_1$ CH_2

The total atomization energy or dissociation energy (D_e) of the reaction $CH_2(\tilde{X}\,^3B_1)\rightarrow C(^3P)+2H(^2S)$, is determined through a valence focal-point analysis (Table VI) and corrections for core correlation (Table VII), relativistic, and adiabatic effects. The corresponding total energies of CH_2,[86] CH, C, and H are provided in the supplementary material.

TABLE VII. Core correlation corrections, in kJ mol^{-1}, to the total atomization energy of $\tilde{X}\,^3B_1$ CH$_2$.[a]

Basis	δ[CCSD]	δ[CCSD(T)]	δ[CCSDT]	
cc-pCVDZ	+1.650	−0.042	+0.001	
cc-pCVTZ	+2.686	−0.094	+0.006	
cc-pCVQZ	+3.313	−0.104	+0.011	
aug-cc-pCVQZ	+3.339	−0.102		
cc-pCV5Z	+3.474	−0.105		
aug-cc-pCV5Z	+3.484	−0.104		
aug-cc-pCV6Z	+3.531	−0.105		
CBS[a56][b]	+3.596	−0.106	[+0.011]	[+3.548]

[a] See footnote a in Table IV.

[b] The complete basis set (CBS) δ[CCSD] and δ[CCSD(T)] values were obtained by a polynomial (X^{-3}) extrapolation of the best two (aug-cc-pCV5Z and aug-cc-pCV6Z) available values, resulting in the CBS[a56] estimates.

A. Valence-only results

Since we have valence-only atomic FCI energies available with basis sets up to aug-cc-pV5Z (see supplementary material) errors in our estimated D_e values are determined by the available molecular energies. At most correlated levels enhancements in the one-particle basis lead to larger atomization energies.

It is clear from the results of Table VI that convergence of the valence atomization energy of ^{3}CH$_2$ at the ROHF level is monotonic and fast, the limiting value of 647.57 kJ mol^{-1}, obtained with and without diffuse functions, is reached within 0.1 kJ mol^{-1} with the cc-pV5Z basis set. The correlation increments converge considerably slower, though changes in the higher-order corrections, those above CCSD(T), seem to be comfortably small. Overall, convergence behavior of the different correlation energy increments is smooth, especially when the basis set contains diffuse functions, and thus the convergence in the CC series is well established, ensuring that our estimate of the valence CBS FCI atomization energy of $794.64^{+0.30}_{-0.50}$ kJ mol^{-1}, obtained by averaging the two CBS FCI values of Table VI, should be highly reliable. The asymmetry of our conservative error estimate is due to the somewhat uncertain extrapolation of the CCSD correlation energy increment.

B. Effect of core correlation

The core-correlation contribution, in kJ mol^{-1}, to the atomization energy of $\tilde{X}\,^3B_1$ CH$_2$ has been given as +3.05 by Grev and Schaefer (GS),[117] determined with medium-size basis CCSD(T) calculations, +3.31 by Parthiban and Martin,[11] obtained as part of their model chemistry calculations, and +3.52 by Partridge.[51]

The value established in this study (cf. Table VII) basically confirms these earlier results, the converged estimate being $+3.50\pm0.10$ kJ mol^{-1}.

C. Relativistic and adiabatic effects

Most standard electronic structure calculations, including the ones used here, are not designed to describe the lowest energy spin multiplet of atomic states. In these cases the computed energy is a weighted average of all the available multiplet states. To correct for this deficiency of our electronic structure computations, we take the atomic first-order spin–orbit correction of −0.33 kJ mol^{-1} (−28 cm^{-1}) for C(^3P) based on excitation energies reported by Moore[118] but employ no correction for ^{3}CH$_2$. This results in an increase of the binding energy. The MVD1 relativistic energy correction to D_e of ^{3}CH$_2$, computed at the cc-pCV5Z CCSD(T) level, is −0.293 kJ mol^{-1}. Therefore, the overall relativistic correction to the atomization energy of ^{3}CH$_2$ is -0.62 ± 0.20 kJ mol^{-1}.

The DBOC correction, computed at the TZ2P+f SCF level, increases the total atomization energy by +0.203 kJ mol^{-1}. A conservative error estimate of ±0.1 kJ mol^{-1} may be attached to this value.

D. Total atomization enthalpy

Using the converged estimates from the previous subsections, one arrives at the value of $D_e(\tilde{X}\,^3B_1\mathrm{CH}_2) = 794.64^{+0.30}_{-0.50} + 3.50^{+0.10}_{-0.10} - 0.62^{+0.20}_{-0.20} + 0.20^{+0.10}_{-0.10} = 797.72^{+0.39}_{-0.59}$ kJ mol^{-1}. Obviously, this value needs to be corrected with the ZPE of the triplet state, $44.69^{+0.18}_{-0.18}$ kJ mol^{-1}, cf. Sec. III, before comparison with experiment becomes possible, yielding $753.03^{+0.43}_{-0.62}$. The best experimental value we are aware of, with no error bar quoted, is 753.3 kJ mol^{-1}.[25]

VI. FIRST BOND DISSOCIATION ENERGY OF ^{3}CH$_2$

The change in the internal energy during the dissociation process CH$_2$→CH+H is called the first bond dissociation energy (BDE) (Ref. 22) of CH$_2$, $D^{\mathrm{o}}_{U1}(T)$(CH–H), and it is given as the energy difference of the appropriate species in their respective ground states. Our calculated focal-point results for D^{o}_{U1} are collected in Tables VIII and IX for the valence-only and core-valence treatments, respectively. As it is seen in Table VIII convergence of the valence-only D^{o}_{U1} is considerably faster than convergence of D_e (see Table VI), making the converged CBS FCI estimate very reliable. The only further notable characteristics of these tables are as follows: (1) The cc-pVXZ ROHF results do not but the augmented basis set ROHF results do show smooth convergence toward the HF limiting value of 408.13 ± 0.05 kJ mol^{-1}. (Nevertheless, the aug-cc-pVDZ ROHF estimate is farther away from the limit by almost 3 kJ mol^{-1} than the cc-pVDZ ROHF value.) (2) The correlation corrections obtained with the DZ basis sets are somewhat unreliable both with and without augmentation.

Our valence-only CBS FCI estimate is 442.91 ±0.25 kJ mol^{-1}. Our core-valence correction estimate (see Table IX) is 2.79 ± 0.10 kJ mol^{-1}.

Appending relativistic and DBOC corrections, computed at the cc-pCVQZ CCSD(T) and TZ2P+f HF levels, respectively, to these computed values results in $442.91^{+0.25}_{-0.25} + 2.79^{+0.10}_{-0.10} - 0.44^{+0.10}_{-0.10} + 0.34^{+0.10}_{-0.10} = 445.60\pm0.30$ kJ mol^{-1}. (The DBOC corrections for H, CH, and ^{3}CH$_2$ are 59.7, 441.7, and 472.8 cm^{-1}, respectively. The correlation contribution to the relativistic correction is only −0.06 kJ mol^{-1}.)

TABLE VIII. Valence focal-point analysis of the bond dissociation energy of $\tilde{X}\,{}^3B_1$ CH_2 in kJ mol^{-1}.[a]

Basis	HF	δ[CCSD]	δ[CCSD(T)]	δ[CCSDT]	δ[FCI]	FCI
cc-pVDZ(5/14)	402.63	+23.64	−0.28	−0.37	+0.01	425.63
cc-pVTZ(14/30)	408.13	+31.79	+0.21	−0.40	−0.06	439.67
cc-pVQZ(30/55)	408.22	+34.01	+0.33	−0.43	[−0.06]	[442.07]
cc-pV5Z(55/91)	408.23	+34.48	+0.35	[−0.43]	[−0.06]	[442.57]
cc-pV6Z(91/140)	408.15	+34.62	+0.35	[−0.43]	[−0.06]	[442.63]
CBS[456]	[408.15]	+34.81	+0.35	[−0.43]	[−0.06]	[442.82]
aug-cc-pVDZ(9/23)	399.69	+24.38	−0.18	−0.40	−0.03	423.46
aug-cc-pVTZ(23/46)	407.30	+32.08	+0.22	−0.44		
aug-cc-pVQZ(46/80)	407.91	+34.09	+0.34			
aug-cc-pV5Z(80/127)	408.11	+34.51	+0.34			
aug-cc-pV6Z(127/189)	408.13	+34.67	+0.35			
CBS[a456]	408.13	+34.89	+0.36	[−0.44]	[−0.03]	[442.91]

[a] After each basis set the number of contracted Gaussian basis functions for H/C is given in parentheses. See footnote a in Table IV for details.

The ZPE correction of this value is $-27.75^{+0.19}_{-0.19}$ kJ mol^{-1}. Therefore, the zero-point energy corrected bond dissociation energy is $417.85^{+0.35}_{-0.35}$ kJ mol^{-1}.

VII. ENTHALPIES OF FORMATION

With all the high-quality *ab initio* results at hand from previous sections we can calculate the enthalpy of formation of $\tilde{X}\,{}^3B_1$ CH_2 in two different ways: one employs the reaction $C+2H\rightarrow CH_2$ while the other uses the reaction $CH+H\rightarrow CH_2$.

Calculation of the enthalpy of formation from the computed internal energies requires knowledge of the enthalpy of formation of the atoms H and C and of $CH(^2\Pi)$ in their respective ground electronic states. The relevant atomic data, when available, were taken from Ref. 20 and are given, in kJ mol^{-1}, as $\Delta_f H^{\circ}_{298}[C(^3P)]=716.68\pm 0.45$, $\Delta_f H^{\circ}_{298}[H(^2S)]=217.998\pm 0.006$, $H_{298}-H_0[H]=6.197\pm 0.001$, $H_{298}-H_0[C_{\mathrm{grafite}}]=1.050\pm 0.20$, and $H_{298}-H_0[C_{\mathrm{gas}}]=6.536\pm 0.001$. Furthermore, $H_{298}-H_0[H_2]=8.468\pm 0.001$,[20] $H_{298}-H_0[CH(^2\Pi)]=8.730$ kJ mol^{-1},[19] and $H_{298}-H_0[^3CH_2]=9.94$ kJ mol^{-1}.[25] The resulting 0 K atomic enthalpies of formation are $\Delta_f H^{\circ}_0[H(^2S)]=216.034\pm 0.006$ kJ mol^{-1} and $\Delta_f H^{\circ}_0[C(^3P)]=711.19\pm 0.45$ kJ mol^{-1}. For $CH(^2\Pi)$ the best recommended values[13] for $\Delta_f H^{\circ}_0$ and $\Delta_f H^{\circ}_{298}$ are $592.47^{+0.56}_{-0.47}$ and $595.73^{+0.56}_{-0.47}$ kJ mol^{-1}, respectively. The ZPE of $^2\Pi$ CH is 16.941 ± 0.010 kJ mol^{-1}.[13]

TABLE IX. Core correlation corrections, in kJ mol^{-1}, to the bond dissociation energy of $\tilde{X}\,{}^3B_1$ CH_2.[a]

Basis	δ[CCSD]	δ[CCSD(T)]	δ[CCSDT]
cc-pCVDZ	+1.152	−0.140	−0.006
cc-pCVTZ	+2.267	−0.265	−0.031
cc-pCVQZ	+2.893	−0.310	−0.043
aug-cc-pCVQZ	+2.906	−0.310	
cc-pCV5Z	+3.045	−0.320	[−0.043]
aug-cc-pCV5Z	+3.051	−0.320	
aug-cc-pCV6Z	+3.096	−0.323	
CBS[a56][b]	+3.158	−0.327	[−0.043]

[a] See footnote a in Table IV.

[b] The complete basis set (CBS) δ[CCSD] and δ[CCSD(T)] values were obtained by a polynomial (X^{-3}) extrapolation of the best two (aug-cc-pCV5Z and aug-cc-pCV6Z) available values, resulting in the CBS[a56] estimates.

Using the first approach, based on the total atomization energy, the calculated quantities of the previous sections relate to the theoretical enthalpy of formation of CH_2 at 0 K via the equation $\Delta_f H^{\circ}_0(^3CH_2)=[\Delta_f H^{\circ}_0(C)+2\Delta_f H^{\circ}_0(H)]+\mathrm{ZPE}(^3CH_2)-D_e$. Therefore, our resulting best estimate for $\Delta_f H^{\circ}_0(\tilde{X}\,{}^3B_1\ CH_2)$ is $1143.26^{+0.45}_{-0.45}+44.69^{+0.18}_{-0.18}-797.72^{+0.39}_{-0.59}=390.23^{+0.76}_{-0.62}$ kJ mol^{-1}.

Using the second approach, based on the bond dissociation energy of CH_2, one obtains $\Delta_f H^{\circ}_0(^3CH_2)=[\Delta_f H^{\circ}_0(CH)+\Delta_f H^{\circ}_0(H)]+\mathrm{ZPE}(^3CH_2)-\mathrm{ZPE}(CH)-D^{\circ}_{U1}$, yielding $808.51^{+0.47}_{-0.56}+44.69^{+0.18}_{-0.18}-16.94^{+0.10}_{-0.10}-445.60^{+0.30}_{-0.30}=390.66^{+0.59}_{-0.67}$ kJ mol^{-1}.

Our best estimate of $\Delta_f H^{\circ}_0(^3CH_2)$ is obtained by averaging the two computed values, resulting in a final value of $390.45^{+0.68}_{-0.64}$. The computed enthalpy of formation at 298.15 K is as follows: $\Delta_f H^{\circ}_{298}(^3CH_2)=390.45^{+0.68}_{-0.64}+(9.94-8.468-1.050)=390.87^{+0.68}_{-0.64}$ kJ mol^{-1}.

It is clear from our previous discussion that the source of the largest possible remaining inaccuracy of our computed value comes from the ZPE estimates (especially that of $^3CH_2$) and from the enthalpy of formation of $C(^3P)$. Without further significant improvements in these quantities the first-principles computation of $\Delta_f H^{\circ}_T$ of the CH_2 radical cannot be improved.

Taking the T_0 value of $3147\pm 5\ cm^{-1}$ (37.646 ± 0.060 kJ mol^{-1}) one obtains the enthalpy of formation of the $\tilde{a}\,{}^1A_1$ state of CH_2 at 0 K as $428.10^{+0.68}_{-0.64}$ kJ mol^{-1}. This way one can avoid the possible problems with the ZPE determination of the lower state.

VIII. CONCLUSIONS

Recent high-level *ab initio* computations of thermochemical quantities (see, e.g., Refs. 12, 13, 17, and 31) proved that in this field of chemical research theory achieved a status whereby it can surpass or at least match the accuracy of (most) experiments. The state-of-the-art computational results presented in this paper for CH_2 nicely support this view.

The computed 0 K and 298 K enthalpies of formation of $\tilde{X}\,^3B_1$ CH_2 are $390.45^{+0.68}_{-0.64}$ and $390.87^{+0.68}_{-0.64}$ kJ mol^{-1}, respectively, while $\Delta_f H_0^o(\tilde{a}\,^1A_1\ CH_2) = 428.10^{+0.68}_{-0.64}$ kJ mol^{-1}. These results are substantially different from some of the enthalpies of formation recommended by high-profile compilations of thermochemical quantities even to warrant reevaluation of modeling studies based on old ''experimental'' thermochemical data. The results, on the other hand, clearly support the recent investigations of Ruscic *et al.*[48] and Willitsch *et al.*,[49] whereby analyses of a local thermochemical network and a correction to the ionization energy of CH_2 resulted in $\Delta_f H_0^o(\tilde{X}\,^3B_1\ CH_2) = 389.87 \pm 0.86$ and 390.73 ± 0.66 kJ mol^{-1}, respectively.

To achieve the claimed high accuracy in the computed enthalpies of formation it was necessary to obtain similar quality results for several other highly interesting and widely studied quantities. First, we arrived at 3262^{+29}_{-16} cm^{-1} for the pure singlet–triplet splitting. After careful consideration of available theoretical and experimental zero-point energy (ZPE) results, we recommend the estimates 3736^{+15}_{-15}, 3612^{+10}_{-10}, and -124^{+18}_{-18} cm^{-1} for ^{3}ZPE, ^{1}ZPE, and ΔZPE $= {}^1\text{ZPE} - {}^3\text{ZPE}$, in order. Therefore, our computed singlet–triplet splitting value is fully consistent with the accurate experimental T_0 estimate[97,98] of 3147 ± 5 cm^{-1}. Second, the total atomization energy obtained in this study is $D_e(\tilde{X}\,^3B_1\ CH_2) = 797.72^{+0.39}_{-0.59}$ kJ mol^{-1}. Third, the 0 K pure bond dissociation energy of $^3CH_2$ was computed to be 445.60 ± 0.30 kJ mol^{-1}.

The source of the largest remaining inaccuracy in our computed effective values comes from the ZPE estimates (especially that of $^3CH_2$). In enthalpy of formation predictions the significant uncertainty in the enthalpy of formation of $C(^3P)$ also hinders further progress. Without significant improvements in these quantities the first-principles computation of $\Delta_f H_T^o$ of the CH_2 radical cannot be improved.

It is perhaps worth pointing out that the most recent modification of the Gaussian-3 procedure, G3-RAD,[64] predicts 389.5 kJ mol^{-1} for $\Delta_f H_{298}^o(\tilde{X}\,^3B_1\ CH_2)$, thus deviating -1.4 kJ mol^{-1} from our computed value. This excellent agreement between the two values is shadowed somewhat by the fact that for $CH(^2\Pi)$ the G3-RAD value deviates -4.7 kJ mol^{-1} from our estimate, $595.93^{+0.47}_{-0.56}$ kJ mol^{-1}.[13]

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