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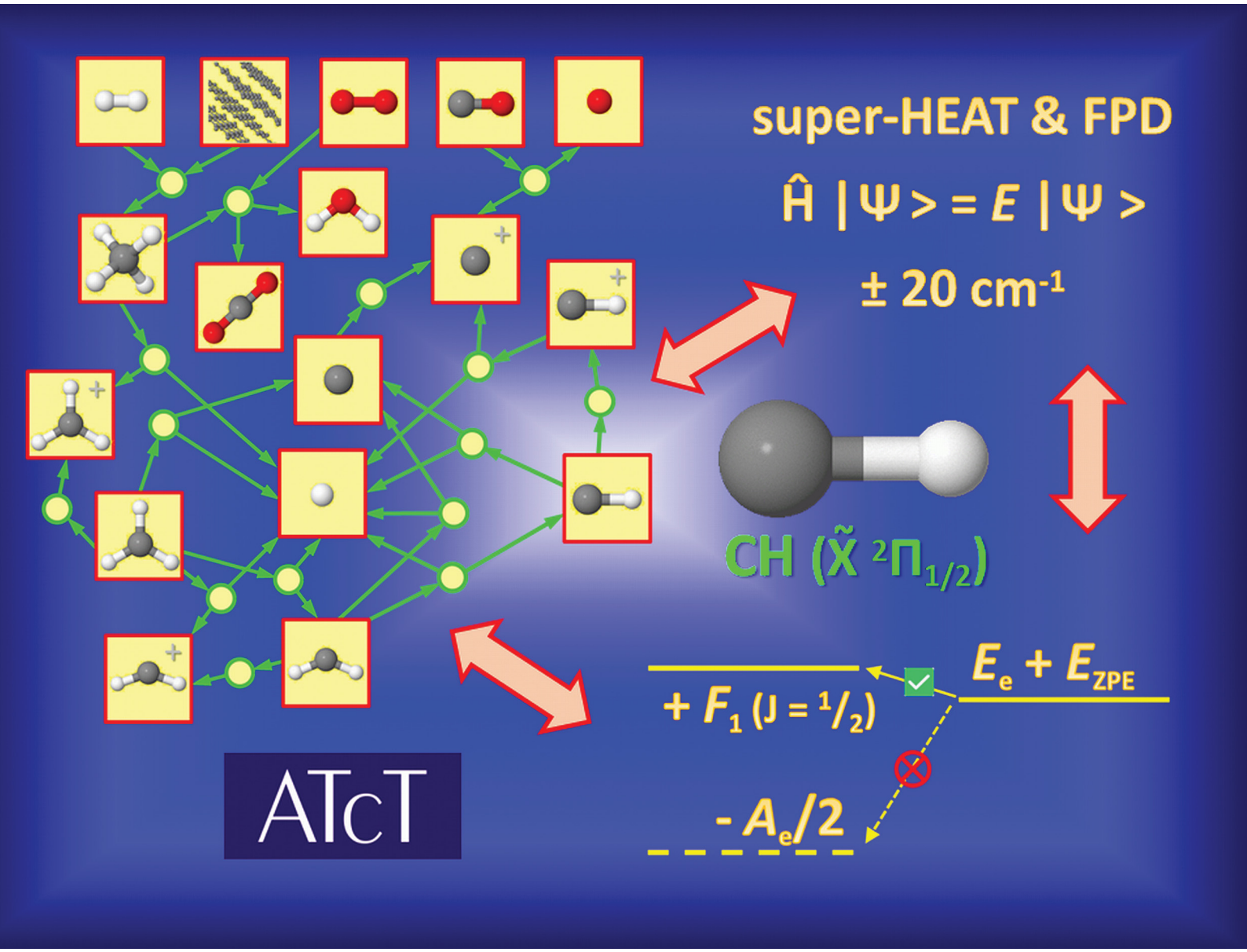

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Sub 20 cm^{-1} computational prediction of the CH bond energy – a case of systematic error in computational thermochemistry†

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The bond dissociation energy of methylidyne, D_0(CH), is studied using an improved version of the High-Accuracy Extrapolated *ab initio* Thermochemistry (HEAT) approach as well as the Feller–Peterson–Dixon (FPD) model chemistry. These calculations, which include basis sets up to nonuple (aug-cc-pCV9Z) quality, are expected to be capable of providing results substantially more accurate than the *ca.* 1 kJ mol^{-1} level that is characteristic of standard high-accuracy protocols for computational thermochemistry. The calculated 0 K CH bond energy (27 954 ± 15 cm^{-1} for HEAT and 27 956 ± 15 cm^{-1} for FPD), along with equivalent treatments of the CH ionization energy and the CH^+ dissociation energy (85 829 ± 15 cm^{-1} and 32 946 ± 15 cm^{-1}, respectively), were compared to the existing benchmarks from Active Thermochemical Tables (ATcT), uncovering an unexpected difference for D_0(CH). This has prompted a detailed reexamination of the provenance of the corresponding ATcT benchmark, allowing the discovery and subsequent correction of a systematic error present in several published high-level calculations, ultimately yielding an amended ATcT benchmark for D_0(CH). Finally, the current theoretical results were added to the ATcT Thermochemical Network, producing refined ATcT estimates of 27 957.3 ± 6.0 cm^{-1} for D_0(CH), 32 946.7 ± 0.6 cm^{-1} for $D_0(CH^+)$, and 85 831.0 ± 6.0 cm^{-1} for IE(CH).

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Introduction

The prediction of molecular bond energies and associated enthalpies of formation represents perhaps the most fundamental area of application for the field of quantum chemistry. While such properties are, in and of themselves, quite important for our understanding of chemical processes, the pursuit of increasingly accurate methods to calculate these quantities has historically driven development of theories for electron correlation,[1–19] construction of basis sets,[20–30] and advanced our understanding of the fundamental nature of, and various contributions to, molecular energies.[31–40]

The usual approaches for calculating relative molecular energies to an accuracy of *ca.* 1 kJ mol^{-1} ("subchemical accuracy") have typically been based on so-called "composite model chemistries", a concept inspired by the work of Pople and collaborators.[41–46] Originally, the aim of the pursuit was to achieve "chemical accuracy", conventionally taken as ±1 kcal mol^{-1}, or about ±4 kJ mol^{-1} (in terms of 95% confidence intervals for the calculated property, which is, by accepted convention, the measure of uncertainties in thermochemistry[47,48]). In order to achieve subchemical accuracy, the exact relativistic energy in a complete basis set is usually estimated by state-of-the-art composite approaches as the sum of contributions for the non-relativistic electronic energy, an incorporation of relativistic effects (scalar relativity and those associated with the spin–orbit interaction), and nuclear motion terms such as the vibrational zero-point energy (ZPE) and the diagonal Born–Oppenheimer correction (DBOC). Broadly speaking, a specific composite model chemistry falls into one of two categories. "Fixed" recipes such as High-Accuracy *ab initio* Extrapolated Thermochemistry (HEAT),[30,49–52] Weizmann-*n* (W *n*),[53–57] and Argonne National Laboratory-*n* (ANL-*n*)[58] are founded upon a particular and precisely-defined treatment of the above energy contributions. By benchmarking calculations against sufficiently accurate thermochemistry for a suitable test suite of species, fixed recipes can be calibrated to establish generic associated statistical uncertainties (known as "Type A" or statistically-based uncertainties[47]), and can be carefully designed

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to facilitate error cancellation. In contrast, "free" recipes, such as Focal Point Analysis (FPA)[59–63] and Feller–Peterson–Dixon (FPD),[29,38,64–67] are adapted to each species in question. By observing the convergence of each energy contribution with respect to level of theory and size of basis set, and estimating its uncertainty (known as "Type B" or experience-based uncertainties[47]), it is possible to control the error of these recipes for a specific species to achieve a fixed objective of accuracy (provided the calculations are computationally feasible).

As time passes and computational capabilities (software and hardware) improve, new model chemistries (or modifications to extant recipes) are developed to either increase the chemical space spanned by an old recipe or to improve upon its accuracy. The Active Thermochemical Tables (ATcT) approach, which is based on a unique paradigm that enables the derivation of accurate, reliable, robust, and internally consistent thermochemistry,[68–70] has played a key role in the development and benchmarking of a number of sub-kJ mol^{-1} theoretical approaches.[29,30,49–52,55,56,58,71–74] The ATcT approach is based on constructing, statistically analyzing, and solving a Thermochemical Network (TN), which contains all available high-quality information from both experiments and high-level theoretical treatments. For many small molecular species, there is sufficient high-quality experimental data that allows the ATcT approach to provide uncertainties far tighter than the accuracy of quantum-chemical computations, and thus is the measure against which these methods can be calibrated. However, there are exceptions where computed values provide most of the foundation for an ATcT enthalpy of formation, an example being the title molecule of this work. This is not necessarily a cause for concern, provided that the stated uncertainties of the theoretical predictions incorporated in the TN are an accurate reflection of the 95% confidence interval for the calculated property. However, particularly in computational thermochemistry, there is always an underlying danger that unknown systematic errors may be present. Such is the case for methylidyne (CH).

In the course of ongoing work intended to extend the HEAT protocol[30] to target *ca.* 20 cm^{-1} accuracy (provisionally termed "semi-spectroscopic"), the computed bond dissociation energy of methylidyne, D_0(CH), was benchmarked against the most recent ATcT values of 27 970.5 ± 7.3 cm^{-1} [75] or 27 971.0 ± 7.3 cm^{-1}.[70] It was found that the new, very high-level theoretical value was lower than the ATcT estimate by *ca.* 16–17 cm^{-1}, and by an additional *ca.* 4 cm^{-1} from the even earlier ATcT value of 27 974.6 ± 8.4 cm^{-1}.[76] While technically still within the combined uncertainties of the quoted ATcT values and the stated accuracy objective of the protocol, the CH system is sufficiently small so that essentially full CI accuracy in the valence space is readily achieved. Indeed, close examination of the computed bond energy contributions suggested that the procedure was likely within 10 cm^{-1} of convergence, nearly a factor of two better than the apparent overall error in the calculations.

Significantly, the six largest contributors to the provenance of the CH thermochemistry in ATcT TN 1.122r[70] are computational, rather than experimental, studies. As will be discussed in this report, much of the initial discrepancy between the extended HEAT and the available ATcT values for D_0(CH) can be traced to a systematic error arising from improper treatment of rotational-electronic coupling in some of the earlier high-level theoretical values that are incorporated in the ATcT TN.

Namely, the spin–orbit (SO) correction to the computed D_0(CH) has two components: one relates to the dissociation limit and involves the correction for the splitting between the $^3P_{0,1,2}$ states of carbon atom, the other to the molecular spin–orbit interaction in the $^2\Pi_{1/2,3/2}$ ground state of methylidyne. There are no particular issues with the former component, which corresponds to the weighted average of the $^3P_{0,1,2}$ states of carbon atom of 29.59 cm^{-1} [77–79] and lowers the C + H dissociation asymptote by the same amount. However, as pointed out in some of the previous literature,[48,58] the correct molecular spin–orbit contribution to the energy – which must include coupling to the rotational angular momentum, a.k.a. rotational zero-point effect – nearly vanishes for the $^2\Pi$ electronic state of CH (*vide infra*). The common approximation of using half the molecular spin–orbit constant (A_e), which has been apparently used in several of the published theoretical values that contribute to the ATcT value, produces a theoretical D_0(CH) that is systematically too large by *ca.* 14 cm^{-1}. This suggests that a detailed scrutiny of prior theoretical results for D_0(CH) that are incorporated in the ATcT TN is in order, with the hope that incorporating a proper treatment of the molecular spin–orbit effect in calculations that have used the simplified spin–orbit correction might narrow the gap between the provisional semi-spectroscopic HEAT result and ATcT. The purpose of this work is to explore this issue, as well as to provide new computational benchmarks for the ionization energy of CH and the bond energy of the resulting CH^+ ion.

Computational

Extended HEAT calculations

The calculations employed in the extended HEAT treatment are more fully described in ref. 52, but are summarized here and in Table 1. Briefly, the non-relativistic electronic energy is approximated from a series of CCSD(T), CCSDT(Q)$_\Lambda$, and CCSDTQ(P)$_\Lambda$ calculations employing the aug-cc-pCV{8,9}Z, aug-cc-pCV{Q,5}Z, and pVTZ basis sets, respectively, where the {X,Y} notation indicates an $(L+1/2)^{-4}$ extrapolation.[80–84] The very large 9-ζ basis sets for C and H were constructed during the process of this work, and facilitate a very good approximation to the complete basis set limit for the important (non-relativistic) CCSD(T) contribution to the properties studied here. Scalar relativistic effects are accounted for by inspecting the difference between spin-free Dirac Coulomb[85,86] and non-relativistic CCSD(T)/unc-aug-cc-pCVQZ (unc indicating an uncontracted basis) energies.

The goal of an *ab initio* composite chemistry is to determine the electronic energy as accurately as possible for a given degree of computational cost. For molecules, this electronic energy corresponds to the bottom of a potential energy well, which, of

Table 1 Summary of the extended HEAT and FPD calculations of D_0(CH), IE(CH), and $D_0(CH^+)$. Extended HEAT calculations are performed at the geometries discussed in the main text, and employ UHF reference wavefunctions. FPD calculations are performed at the equilibrium geometry for each level of theory/basis, and employ ROHF reference wavefunctions. Basis sets are abbreviated such that aug-cc-pCV*n*Z is written as aCV*n*Z. Calculations performed within the frozen-core approximation are marked with [fc], and core-valence corrections are marked with [cv]. NREE stands for non-relativistic electronic energy. All values are reported in cm^{-1}

Component	Extended HEAT	ΔD_0(CH)	ΔIE(CH)	$\Delta D_0(CH^+)$	FPD	ΔD_0(CH)
SCF	aCV9Z	19 916.1	82 199.2	24 825.3	None	
CCSD(T)	aCV{8,9}Z	9481.6	3606.5	9588.6	[fc] aV{8,9}Z	29 354.2
					[cv] awCV{Q,5}Z	48.6
Post-(T)	$(Q)_\Lambda$–(T)/aCV{Q,5}Z	51.8	49.2	43.7	[fc] T–(T)/aV5Z	31.5
	[fc] $(P)_\Lambda$–$(Q)_\Lambda$/VTZ	1.8	−4.6	8.4	[fc] Q–T/aVQZ	12.6
					[fc] FCI/VQZ	0.3
					[cv] T–(T)/wCVTZ	5.2
					[cv] Q–T/wCVDZ	−0.3
Total NREE		29 451.2	85 850.2	34 465.9		29 452.2
Scalar rel.	SFDC CCSD(T)/unc-aCVQZ	−13.9	−25.9	−20.1	[fc] CCSD(T)-DK/V5Z-DK	−14.0
Rot-spin–orbit	Hill–Van Vleck/atomic exp.	−29.8	−0.2	−42.2	Hill–Van Vleck/atomic exp.	−29.8
DBOC	CCSD/aCVQZ	−36.7	4.9	−41.7	[fc] CCSD/aVTZ	−36.7
	[fc] Q–D/VTZ	−0.8	−0.6	−0.4		
ZPE	Dunham	−1416.1	0.0	−1416.1	Dunham	−1416.1
Total		27 954.0	85 828.7	32 945.5		27 955.6

course, is not an observable. Instead, 0 K thermochemistry refers to the *lowest actually existing* rovibrational energy level.[48] For many polyatomic species, it is entirely sufficient to simply calculate the vibrational zero-point energy (ZPE) by performing a geometry optimization and frequency analysis and, depending on the desired accuracy, further improve the ZPE by explicitly including anharmonic contributions. However, for some species the nominal vibrational ground state does not correspond to the lowest actually existing rovibrational level. There are several potential reasons that can lead to this situation, some of which have been explained in detail elsewhere.[48] For example, the putative lowest rotational level is simply wiped out in some species by nuclear spin statistics, such as in O_2[51,68,87] or CH_3^+.[88] A different type of situation, of particular relevance here, occurs in open-shell chemical species that have a degenerate ground state and undergo a molecular spin–orbit interaction. In a typical computational approach for such cases, the ZPE correction would be augmented by a contribution from molecular spin–orbit coupling, the magnitude of which is frequently taken simply as half the experimentally determined spin–orbit constant A_e. However, this procedure tacitly assumes that the contribution comes entirely from the coupling of the electronic angular momentum to the spin, and that the coupling to the rotational angular momentum is negligible. The latter generally does not hold for small hydrides, which require additional care.

In particular, the detailed coupling of rotational, spin, and electronic angular momenta in diatomics is normally described either *via* pure or intermediate Hund's cases.[89] Bearing some analogy with the cause célèbre of the (inverted) $^2\Pi_i$ ground state of OH,[51,64,65] the coupling pertinent to the regular $^2\Pi_r$ ground electronic state of CH presents a case of spin uncoupling corresponding to the transition from Hund's case (a) to (b), quantitatively described by the $^2\Pi$ Hamiltonian elaborated by Hill and Van Vleck.[89,90] The zero of the energy scale of this Hamiltonian is the hypothetical vibrationless ground level before any coupling of spin and angular momenta is considered, which computationally corresponds to the non-relativistic (*i.e.* spin–orbit averaged) electronic energy corrected for the purely vibrational ZPE. Using the available spectroscopic constants for the $^2\Pi$ state of CH, including A_e = 28.05 cm^{-1},[91–93] the Hill–Van Vleck Hamiltonian indicates that the lowest rotational level, R = 0, N = 1, J = 1/2, is 0.16 cm^{-1} *above* the vibrationless level of the $^2\Pi$ state, rather than $A_e/2$ = 14.02 cm^{-1} *below* it. Ironically, one would be better off by committing the error of altogether ''forgetting'' to consider the molecular spin–orbit of methylidyne, than by including it *via* the simplistic $A_e/2$ approach. Thus, the extended HEAT calculations reported here use the typical weighted-average treatment of the atomic spin–orbit corrections and the Hill–Van Vleck treatment of the CH spin–orbit correction. As the ground state of the CH^+ cation is $^1\Sigma^+$, its first-order spin–orbit coupling is zero.

In addition to the ZPE and spin–orbit corrections (where second-order spin–orbit corrections have been ignored but are expected to be negligible[94]), the computed values also include the diagonal Born–Oppenheimer correction, which is determined using a sequence of CCSD and CCSDTQ wavefunctions with aug-cc-pCVQZ (for the former) and cc-pVTZ (for both) basis sets. The CH vibrational zero-point energy (ZPE) is 1416.07 cm^{-1}, as obtained from the best available spectroscopic parameters[91–93] of the Dunham expansion[95] (including the small Y_{00} term[96] of 1.76 cm^{-1}), while the CH^+ ZPE of 1416.1 cm^{-1} was taken from the work of Cho and Le Roy.[97]

Calculations for CH^+ used the geometry from Cho and LeRoy[97] (1.12846 Å). The CH calculations reported below were

performed at 1.11810 Å, a geometry determined *via* fit of extended HEAT energies calculated at four points around the region of the minimum. This geometry is far away from the value (1.1199 Å) reported by Huber and Herzberg,[93] which is ultimately an interesting consequence of the electronic contribution to the moment of inertia, a point that will be elaborated in a forthcoming publication. However, the difference in D_0(CH) between the Huber and Herzberg and the fit geometries is less than a wavenumber, and thus is not critical to this work.

The CCSDTQ(P)$_\Lambda$ correlation energies and the post-CCSD DBOC contributions were calculated with the MRCC program of Kallay.[98,99] All other calculations employed the CFOUR program suite.[100,101] UHF references were used for all species, with no symmetry equivalencing performed (calculations enforced only D_{2h} symmetry).

Extended FPD calculations

As mentioned previously, the FPD[66,67] approach to thermochemical and spectroscopic properties is a flexible composite model chemistry that seeks to include all physically significant effects judged on a molecule-specific criterion. For example, in the case of a heavy atom diatomic, like HI ($^1\Sigma^+$), the FPD approach would include a second order molecular spin–orbit correction even though for lighter molecules that contribution might prove to be negligible.[94] For even heavier elements relativistic effects are incorporated with a full 4-component treatment.[102] Chemical systems that involve a notable degree of multi-configurational character could require the use of multi-reference singles and doubles configuration interaction (MRSD-CI), as opposed to single reference coupled cluster theory, as the primary level of theory. The FPD approach has been under development for almost 20 years, and, while FPD and HEAT involve some of the same components, details of the former procedure varies from molecule to molecule.

When applied to light main group chemical systems, such as CH, the first step in the FPD approach is a series of valence CCSD(T)(FC) geometry optimizations with the diffuse function augmented correlation consistent basis sets, aug-cc-pV*n*Z, n = D,T,Q...9.[20,21,23,24,82,103] Note that, in general, all FPD components are evaluated at the respective optimal geometries for each basis set/method combination. Exceptions occur when individual energy evaluations require multiple days or weeks of computer time to complete. In such cases geometries are taken from the next closest level of theory. The use of optimal geometries yields accurate equilibrium structures and their associated harmonic vibrational frequencies that have been shown to agree well with experimental (or semi-experimental[104]) r_e structures and ω_i. As will be discussed, the availability of results from multiple basis sets and the resulting uniform convergence pattern makes possible a simple extrapolation to the complete basis set (CBS) limit.

Open shell systems are described with the R/UCCSD(T) method available in the MOLPRO[105–107] program package, which begins with restricted open-shell Hartree–Fock (ROHF) orbitals, but allows a small amount of spin contamination in the solution of the CCSD equations.[108–110] Because MOLPRO only supports up to L_{max} = 6 (i-functions), it was necessary to approximate R/U energies for $L_{max} > 6$ by assuming that the difference between UCCSD(T)(FC) energies, obtained with Gaussian 09, and R/UCCSD(T) energies was constant to 10^{-6} E_h. Atomic calculations imposed an orbital symmetry equivalencing restriction, *i.e.* $p_x = p_y = p_z$.

In order to approximately account for the residual 1-particle basis set incompleteness, a CBS extrapolation formula, $(L_{max} + 1/2)^{-4}$, was applied to the raw energies. There are multiple such formulas in the literature. Examination of the performance of four widely used formulas involving nearly 500 comparisons with reliable estimates of the CBS limit revealed that none of them proved to be superior across all basis sets and molecules studied.[83] Therefore, we take half the spread among four different extrapolation formulas as a crude, conservative estimate of the uncertainty in the CBS dissociation energies. These include both two term (L_{max}^{-3}, $(L_{max} + 1/2)^{-4}$) and three term formulas ($A\exp(-bL_{max})$, $A\exp(-(L_{max}-1)) + B\exp(-(L_{max}-1)^2)$).

While the valence CCSD(T) contribution clearly dominates the FPD calculation of thermodynamic properties, a number of smaller corrections are required in order to achieve uniform accuracy at the highest level. The most important of these is typically the outer-core/valence (CV) correlation correction. CV correlation is determined with R/UCCSD(T) calculations using the aug-cc-pwCV*n*Z, n = 3,4,5 basis sets[25] and incorporates the 1s pair of electrons in first row atoms in the correlation treatment. For elements further down the Periodic Table, only the outermost core electrons are included, for example $2s^2$ $2p^6$ in sulfur. The CV component is also extrapolated to the CBS limit. A simplistic definition of the valence electron space obtained from a casual examination of the Periodic Table can be inadequate for practical use. For example, in order to achieve quantitative accuracy in CV corrections to binding energies, it has been found necessary to include the first set of "core" electrons in the valence space. This is the case for compounds containing transition metals and heavier elements. The motivation for decomposing the CCSD(T) correlation energy into valence and CV pieces is the desire to avoid costly CV calculations with large basis sets. This savings comes at the cost of assuming additivity in the valence and CV components.

Higher order correlation recovery beyond CCSD(T) was achieved with CCSDT and CCSDTQ using awCV5Z and awCVQZ basis sets, respectively. In the case of a small diatomic like CH, which possesses only five valence electrons, it was also possible to carry out full configuration interaction (FCI) calculations with the VQZ basis set.

Scalar relativistic (SR) contributions to the binding energy were obtained with second-order Douglas–Kroll–Hess (DKH) R/UCCSD(T)(FC)-DK calculations with the aV5Z-DK basis set[111] which was recontracted specifically for DKH.[111–113] The SR correction is insensitive to the quality of the 1-particle and n-particle expansions.

Hydrogen-containing molecules can display a significant (>0.1 kcal mol^{-1} for atomization energies) diagonal

corrections to the Born–Oppenheimer (DBOC) approximation. In the FPD approach as applied to CH we describe this effect with UCCSD-DBOC(FC)/aVTZ calculations. Even triple zeta basis sets have been found to yield nearly converged results.

The FPD and extended HEAT results reported in this work use an identical treatment of the spin–orbit coupling and vibrational zero-point energy effects; this approach results in essentially exact treatments of these contributions to the CH bond energy.

Results and discussion

New computational benchmarks for CH and CH^+

Table 1 summarizes the new FPD and HEAT benchmarks for the bond dissociation energy of methylidyne, D_0(CH), and additionally details the extended HEAT values for the adiabatic ionization energy of methylidyne, IE(CH), and the dissociation energy of methyliumylidene, $D_0(CH^+)$.

One striking feature of Table 1 is the *ca.* 2 cm^{-1} agreement between the FPD and extended HEAT predictions of D_0(CH), particularly in the sum of the non-relativistic electronic-energy (NREE) components. The details of the FPD and extended HEAT calculations differ in a few ways: FPD utilizes core-valence separation where extended HEAT does not, FPD evaluates each component at the equilibrium geometry for that level of theory and basis set where HEAT performs all calculations at a single geometry, FPD employs an ROHF reference where HEAT employs UHF, *etc.* At the end of the day, however, both of these methods are designed to closely approximate (or converge towards) a nearly exact treatment of molecular bond energies, provided that enough computational effort can be expended. In the case of CH, where the NREE components of the electronic energy are relatively well-behaved and the valence full-CI limit is well within reach of modern algorithms and hardware, the current FPD and extended HEAT approaches agree for the bond energy of CH to a remarkable degree. Of note, however, is that both calculations disagree with previous ATcT determinations for the CH bond energy, a point discussed further below.

A detailed breakdown of the various contributions to the extended HEAT calculations is provided in Tables 2–5. As was observed in ref. 30 for HF, CO, N_2, and H_2O, the spin-free relativistic (Table 2) and DBOC (Table 3) components of the calculated properties seem very well converged. Despite the fact that spin-free relativistic contributions to the total energies converge slowly with respect to single-particle basis set size, the increment between the uncontracted aug-cc-pCVTZ and aug-cc-pCVQZ basis sets is less than 0.2 cm^{-1} for all three energy differences. The vibrational ZPE and the combined spin–orbit and rotational contributions (*vide supra*), which come from experimental values or empirical potential energy surfaces, are also essentially exact.

From the above, it can be expected that the overwhelming majority of error in the calculations will come from the non-relativistic electronic energy, the contributions to which are listed in Tables 4 and 5. These certainly appear to be converged to better than 5 cm^{-1}. Even the CCSD correlation energy contribution to the bond energy of CH – known to be the most difficult to converge with respect to single-particle basis set – differs by at most 1 cm^{-1} between extrapolations with the aug-cc-pCV6Z, -7Z, -8Z, and -9Z basis sets. The IE(CH) and $D_0(CH^+)$ are slightly less well behaved, but all extrapolations beyond aug-cc-pCV5,6Z differ by less than 3 cm^{-1}, indicating these values are quite close to the basis set limit. The post-CCSD(T) contributions are also apparently tightly converged, with the basis-set dependence of the T–(T) contribution being the only term with an uncertainty larger than 1 cm^{-1}. Given the small magnitude of the $(P)_\Lambda$–$(Q)_\Lambda$ valence-correlation increment, it is unlikely that correlation beyond CCSDTQ$(P)_\Lambda$ needs to be considered. In this context, it should be noted that the species considered here have at most seven electrons, so CCSDTQ$(P)_\Lambda$ is essentially equivalent to full configuration interaction in the valence space.

With all the composite contributions totalled, the extended HEAT bond dissociation energy of methylidyne is D_0(CH) = 27 954 cm^{-1}, the adiabatic ionization energy of methylidyne is IE(CH) = 85 829 cm^{-1}, and the bond dissociation energy of the corresponding cation, methyliumylidene, is $D_0(CH^+)$ is 32 945 cm^{-1}. We assign these values a rather conservative confidence interval of ±15 cm^{-1}. The agreement of the CH cation bond energy with the value obtained from Cho and Le Roy[97] (32 945 cm^{-1} *vs.* 32 946 cm^{-1}) is outstanding, although

Table 2 Convergence of the relativistic components of the extended HEAT treatment of D_0(CH). Spin-free components are calculated as the difference between a spin-free Dirac Coulomb energy and the equivalent non-relativistic energy. The spin–orbit correction comes from a weighted average of the experimental spin-splittings for the atoms and the Hill–Van Vleck Hamiltonian for $^2\Pi$ CH. Post Hartree–Fock values indicate the contribution from electron correlation only. Basis sets are abbreviated such that aug-cc-pCV*n*Z is written as aCV*n*Z. Uncontracted basis sets are indicated with unc-. Estimated uncertainties are reported in parenthesis. All values are reported in cm^{-1}

Component	Calculation	ΔD_0(CH)	ΔIE(CH)	$\Delta D_0(CH^+)$
Spin-free	SCF/unc-aCVTZ	−15.6	−30.9	−22.8
	SCF/unc-aCVQZ	−15.6	−30.7	−22.8
	CCSD/unc-aCVTZ	1.7	4.5	3.0
	CCSD/unc-aCVQZ	1.6	4.4	2.8
	(T)–D/unc-aCVTZ	0.1	0.4	−0.1
	(T)–D/unc-aCVQZ	0.1	0.5	−0.1
	Total	−13.9 (±0.2)	−25.9 (±0.2)	−20.1 (±0.1)
Rot-spin–orbit	Exp. & Hill–Van Vleck	−29.8 (±0.0)	−0.2 (±0.0)	−42.2 (±0.0)

Table 3 Convergence of the DBOC and vibrational ZPE components of the extended HEAT treatment of D_0(CH), IE(CH), and D_0(CH^+). Vibrational ZPE values for CH come from the Dunham Expansion with data taken from Zachwieja,[91] while the ZPE for CH^+ comes from the work of Cho and Le Roy.[97] Post-SCF DBOC contributions are taken as the difference between the DBOC contributions calculated with the two indicated wavefunctions. Calculations performed in the frozen-core approximation are indicated with [fc]. Basis sets are abbreviated such that aug-cc-pCV*n*Z is written as aCV*n*Z. Estimated uncertainties are reported in parenthesis. All values are reported in cm^{-1}

Component	Calculation	CH ΔD_0	CH ΔIE	CH^+ ΔD_0
DBOC	SCF/aCVTZ	−29.2	1.3	−29.1
	SCF/aCVQZ	−29.3	1.2	−29.2
	CCSD/aCVTZ	−7.8	3.6	−12.8
	CCSD/aCVQZ	−7.4	3.7	−12.5
	[fc] T–D/VDZ	−0.7	−0.8	−0.2
	[fc] T–D/VTZ	−0.8	−0.7	−0.2
	[fc] Q–T/VDZ	−0.1	0.1	−0.2
	[fc] Q–T/VTZ	−0.1	0.1	−0.2
	Total	−37.5 (±0.5)	4.4 (±0.3)	−42.0 (±0.3)
ZPE	Dunham/ empirical	−1416.1 (±1.0)	0.0 (±1.0)	−1416.1 (±1.0)

neglect of contributions such as second-order spin–orbit coupling suggests that asserting any fundamental meaning to agreement within 2 cm^{-1} is likely not well-founded.

Benchmarking the benchmark and updating the ATcT thermochemical network

As mentioned above, the best ATcT value available prior to the commencement of this study and considered as the initial benchmark was D_0(CH) = 27 971.0 ± 7.3 cm^{-1}.[70] In contrast, as detailed in the previous section, the extended HEAT protocol produced D_0(CH) = 27 954 ± 15 cm^{-1}, or 17 cm^{-1} less.

The discrepancy surrounding D_0(CH) was a bit of a surprise and prompted additional four-pronged action, carried out in parallel: (1) a careful reanalysis of the enhanced HEAT procedure and of all the components of the final theoretical value, (2) an entirely independent recalculation of D_0(CH) using the FPD approach, (3) additional enhanced HEAT computations of the components of the positive ion thermodynamic cycle that can lead to D_0(CH) *via* IE(CH) and D_0(CH^+), and (4) a careful analysis of the provenance of the ATcT value.

Additional scrutiny of all the components of the final theoretical value obtained by the enhanced HEAT procedure (which are detailed above) did not turn up any obvious suspects. Furthermore, the independently computed FPD bond dissociation energy of CH was essentially the same as the extended HEAT value (*vide supra*), differing from the cited ATcT value by 15 cm^{-1}. At the same time, the extended HEAT value for D_0(CH^+) = 32 945 cm^{-1} was essentially identical to the ATcT value from the same version,[70] D_0(CH^+) = 32 946.6 ± 2.2 cm^{-1}, with the determination by Hechtfischer *et al.*[114] of D_0(CH^+) = 32 946.7 ± 2.2 cm^{-1} as the leading contributor, further confirmed by the even more accurate subsequent determination by Cho and Le Roy[97] of D_0(CH^+) = 32 946.7 ± 0.6 cm^{-1}. (Note that the latter determination was included in the subsequent ATcT TN ver. 1.130,[115] further tightening the uncertainty of the ATcT value to ±0.6 cm^{-1}, without changing the value itself.)

Table 4 Convergence of the non-relativistic electronic energy components of the extended HEAT treatment of D_0(CH), IE(CH), and D_0(CH^+) through CCSD(T). All post-SCF values are from electron correlation only. Basis sets are abbreviated such that aug-cc-pCV*n*Z is written as aCV*n*Z, and aCV{*n*,*m*}Z indicates a value obtained *via* the $(L+1/2)^{-4}$ extrapolation formula. Estimated uncertainties are reported in parenthesis. All values are in cm^{-1}

Component	Calculation	ΔD_0(CH)	ΔIE(CH)	ΔD_0(CH^+)
SCF	aCVTZ	19 880.7	82 166.2	24 799.8
	aCVQZ	19 909.7	82 192.9	24 816.4
	aCV5Z	19 915.0	82 198.8	24 825.5
	aCV6Z	19 915.8	82 199.3	24 825.3
	aCV7Z	19 916.0	82 199.2	24 825.3
	aCV8Z	19 916.1	82 199.2	24 825.3
	aCV9Z	19 916.1 (±0.0)	82 199.2 (±0.0)	24 825.3 (±0.1)
CCSD	aCVTZ	8643.3	2945.8	8776.1
	aCVQZ	8972.8	3186.9	9117.3
	aCV5Z	9069.5	3262.4	9217.8
	aCV6Z	9108.5	3292.7	9258.4
	aCV7Z	9128.4	3307.1	9279.3
	aCV8Z	9138.9	3314.8	9290.0
	aCV9Z	9145.1	3319.4	9296.6
	aCV{T,Q}Z	9163.0	3326.0	9314.2
	aCV{Q,5}Z	9148.0	3323.7	9299.5
	aCV{5,6}Z	9149.5	3324.7	9301.1
	aCV{6,7}Z	9154.1	3325.6	9306.3
	aCV{7,8}Z	9155.0	3326.7	9306.6
	aCV{8,9}Z	9156.1 (±2.2)	3327.6 (±1.8)	9308.3 (±3.3)
(T)–D	aCVTZ	305.1	253.5	257.5
	aCVQZ	319.0	270.4	272.7
	aCV5Z	322.8	275.0	277.1
	aCV6Z	324.1	276.8	278.7
	aCV7Z	324.7	277.7	279.4
	aCV8Z	325.0	278.1	279.7
	aCV9Z	325.2	278.4	279.9
	aCV{T,Q}Z	327.0	280.1	281.4
	aCV{Q,5}Z	325.9	278.8	280.6
	aCV{5,6}Z	325.4	278.7	280.3
	aCV{6,7}Z	325.5	278.9	280.3
	aCV{7,8}Z	325.5	278.8	280.3
	aCV{8,9}Z	325.5 (±0.1)	278.9 (±0.3)	280.3 (±0.1)

In view of the fact that there are no direct high-accuracy experimental determinations of IE(CH) (the most recent direct determination being 85 817 ± 65 cm^{-1},[116] preceded by 85 850 ± 100 cm^{-1} [117]), and that the ATcT value for IE(CH) is consequently heavily influenced by the difference between the ATcT values for D_0(CH^+), D_0(CH), and IE(C) = 90 820.36 ± 0.06 cm^{-1} [70] – obeying the thermodynamic identity IE(CH) + D_0(CH^+) = IE(C) + D_0(CH) – it is not surprising that the ATcT value[70] for IE(CH) = 85 844.6 ± 7.6 cm^{-1} and the corresponding extended HEAT value differ by 16 cm^{-1}, essentially the same as the difference observed for D_0(CH) itself, and with a consistent sign.

The above findings cast suspicion on the thermochemical determinations that are responsible for the provenance of the ATcT bond dissociation energy of CH (and indirectly for the adiabatic ionization energy of CH) and strongly advised their careful inspection. In this respect, the first important

Table 5 Convergence of the post-CCSD(T) non-relativistic electronic energy components of the extended HEAT treatment of D_0(CH), IE(CH), and $D_0(CH^+)$. Calculations performed within the frozen-core approximation are indicated with [fc]. All post-SCF values are from electron correlation only. Basis sets are abbreviated such that aug-cc-pCV*n*Z is written as aCV*n*Z, and aCV{*n*,*m*}Z indicates a value obtained *via* the $(L+1/2)^{-4}$ extrapolation formula. Estimated uncertainties are reported in parenthesis. All values are in cm^{-1}

Component	Calculation	ΔD_0(CH)	ΔIE(CH)	$\Delta D_0(CH^+)$
T–(T)	aCVTZ	40.9	56.3	25.1
	aCVQZ	41.1	51.7	25.2
	aCV5Z	40.6	49.2	24.6
	aCV{T,Q}Z	41.2	49.0	25.3
	aCV{Q,5}Z	40.2 (±2.0)	47.1 (±3.8)	24.0 (±2.6)
$(Q)_\Lambda$–T	aCVTZ	10.2	0.3	18.6
	aCVQZ	11.1	1.5	19.4
	aCV5Z	11.3	1.8	19.5
	aCV{T,Q}Z	11.6	2.3	19.8
	aCV{Q,5}Z	11.5 (±0.2)	2.0 (±0.3)	19.7 (±0.2)
[fc] $(P)_\Lambda$–$(Q)_\Lambda$	VDZ	1.9	−4.5	8.2
	VTZ	1.8 (±0.2)	−4.6 (±0.2)	8.4 (±0.2)

observation is that although the ATcT TN contains several experimental measurements of D_0(CH),[117–123] these are of rather limited accuracy, and thus the most influential contributors to the ATcT value (as obtained through the variance decomposition analysis[87]) are high-level theoretical calculations extracted from the literature[29,36,39,49,51,54,55,58,71,82,124–134] and inserted in the ATcT TN. The second relevant observation is that the difference between the enhanced HEAT computation and the quoted ATcT value appears to suspiciously correspond both in sign and (approximately) in size to the systematic error that would be introduced in a theoretical treatment that would use $A_e/2$ as a spin–orbit correction for D_0(CH).

A detailed scrutiny of the individual components of each of the composite calculations extant in the ATcT TN and related to CH was rendered somewhat challenging by the fact that in some of the original theoretical reports not all of the computational components were given explicitly, thus requiring that these be inferred by reverse engineering and/or consulting other studies from the same research group. Nevertheless, the analysis demonstrated that only a small minority of calculations[29,58,133] employed the correct approach to the molecular spin–orbit correction for D_0(CH) (or simply reported D_e(CH) rather than D_0(CH)[131,132]). However, the majority of ATcT TN entries related to CH that are based on high-level calculations[36,39,49,51,54,55,71,82,124–130] required a replacement of the original $A_e/2$ spin–orbit component in the reported calculated value. Admittedly, the size of this *post-factum* correction is in most cases significantly smaller than the individual uncertainties of these calculations, the only exception being the leading FPA calculation[124] (reporting $27\,982^{+11}_{-28}$ cm^{-1}), in which the systematic error and declared uncertainty are of comparable size. However, the use of $A_e/2$ does represent a recurring systematic error, which will have a strong tendency to influence the resulting ATcT value through a cumulative effect.

Indeed, after modifying the most recent developmental version of the TN, ATcT TN ver. 1.130,[115] to create an updated version 1.130a of the ATcT TN, the resulting ATcT value for the bond dissociation energy of CH became D_0(CH) = 27 961.0 ± 8.0 cm^{-1}, a shift downwards by about 10 cm^{-1}. Noting that this shift is still contained within the combined uncertainties of the original ATcT benchmark (27 971.0 ± 7.3 cm^{-1} [70]) and the amended ATcT value, the correction of the systematic error in previous computations reduces the difference between the extended HEAT value and the amended ATcT value to 7 cm^{-1}, which is well within the desired target accuracy of the extended HEAT result.

Generally speaking, developing and benchmarking a new high-accuracy computational protocol using ATcT thermochemical quantities is essentially a two-way road.[48] Namely, the ATcT values are at first used to obtain an estimate of the expected accuracy of the new protocol. Under ordinary circumstances, once the expected accuracy of the new theoretical approach is understood, the computational results obtained using the new protocol can be used to expand and significantly enrich the ATcT TN, further improving both the ATcT results and the original computational values, primarily because the ATcT TN is capable of incorporating thermochemically relevant determinations irrespective of whether they were generated by actual (experimental) or virtual (computational) measurements – as long as the latter can be qualified by realistic uncertainty intervals. Indeed, after generating a new version of ATcT TN (ver. 1.140) by adding the current computational results for D_0(CH) (from both the extended HEAT and FPD approaches), $D_0(CH^+)$, and IE(CH), the final ATcT values are: D_0(CH) = 27 957.3 ± 6.0 cm^{-1} (a further reduction by 3.7 cm^{-1}, accompanied by an improvement in the uncertainty), $D_0(CH^+)$ = 32 946.7 ± 0.6 cm^{-1}, and IE(CH) = 85 831.0 ± 6.0 cm^{-1}. These correspond to the following standard enthalpies of formation at 0 K (298.15 K): $\Delta_f H^\circ$ (CH) = 592.979 (596.314) ± 0.081 kJ mol^{-1}, $\Delta_f H^\circ$ (CH^+) = 1619.746 (1623.090) ± 0.041 kJ mol^{-1}. These, as well as related enthalpies of formation at 0 K and 298.15 K obtained from ATcT TN ver. 1.140 relevant to the broader CH_n, n = 4–0, group of chemical species, are given in Table 6, while the corresponding adiabatic ionization energies, adiabatic electron affinities, and relevant 0 K bond dissociation energies are given in Table 7.

Rarely, the benchmarking procedure itself may already provide some useful feedback to ATcT even before the just described expansion of the ATcT TN with new computational results, as was demonstrated in the present study. Namely, if one of the ATcT benchmark values differs from the corresponding computed values by more than the expected amount and thus effectively represents an outlier, baring the possibility that the particular chemical species in question happens to be a pathological case within the framework of the benchmarked procedure, such an occurrence may well imply that one or more determinations governing the provenance of the corresponding ATcT values may be in error. Earlier, there were at least three cases where highly accurate FPD-type computations helped demonstrate that the accepted thermochemical value, based

Table 6 ATcT values for the enthalpies of formation $\Delta_f H^\circ$ of CH_n (n = 4–0) species and their ions at 0 K and 298.15 K, in units of kJ mol^{-1}, using ATcT TN ver. 1.140. Note that the 298.15 K enthalpies of formation of ions are given within the stationary electron convention[48]

Quantity	0 K	298.15 K	Uncert.
$\Delta_f H^\circ$ (CH_4)	−66.550	−74.519	±0.044
$\Delta_f H^\circ$ (CH_4^+)	1150.679	1144.296	±0.057
$\Delta_f H^\circ$ (CH_3)	149.872	146.472	±0.050
$\Delta_f H^\circ$ (CH_3^+)	1099.346	1095.402	±0.045
$\Delta_f H^\circ$ (CH_3^-)	141.15	137.71	±0.24
$\Delta_f H^\circ$ ($^3CH_2$)	391.063	391.609	±0.094
$\Delta_f H^\circ$ ($^1CH_2$)	428.72	429.13	±0.11
$\Delta_f H^\circ$ (CH_2^+)	1393.20	1394.06	±0.10
$\Delta_f H^\circ$ (CH_2^-)	328.17	328.60	±0.18
$\Delta_f H^\circ$ (^2CH)	592.979	596.314	±0.081
$\Delta_f H^\circ$ (^4CH)	664.70	668.04	±0.52
$\Delta_f H^\circ$ (CH^+)	1619.746	1623.090	±0.041
$\Delta_f H^\circ$ (CH^-)	475.77	479.09	±0.21
$\Delta_f H^\circ$ (C)	711.389	716.874	±0.040
$\Delta_f H^\circ$ (C^+)	1797.842	1803.440	±0.040
$\Delta_f H^\circ$ (C^-)	589.613	594.759	±0.041
$\Delta_f H^\circ$ (H)	216.034	217.998	±0.000
$\Delta_f H^\circ$ (H^+)	1528.084	1530.047	±0.000
$\Delta_f H^\circ$ (H^-)	143.264	145.228	±0.000

on apparently accurate experimental data, is in error (spectroscopic D_0(OH) and the resulting D_0(H–OH), with new experimental data using photoionization mass spectrometry augmented with high-level theory;[64,65] the enthalpy of formation of gas-phase hydrazine[135] and the enthalpy of formation of gas-phase oxalic acid,[136] both of which were originally based on experimental combustion calorimetry of the condensed phase combined with the corresponding vaporization enthalpy). However, the present study is the first case where we were able to demonstrate that a substantial number of ostensibly highly accurate theoretical results had, in common, a hidden systematic error.

Table 7 ATcT values for adiabatic ionization energies (IE), adiabatic electron affinities (EA), and 0 K bond dissociation energies (D_0), related to CH_n (n = 4–0) species and their ions, all in units of cm^{-1}, using ATcT TN ver. 1.140. Note that IE(^{4}CH) and D_0($^1CH_2$ to ^{4}CH), while thermodynamically valid quantities, correspond to spectroscopically forbidden processes

Quantity	Value	Uncert.
IE(CH_4)	101752.4	±3.0
IE(CH_3)	79369.7	±2.0
IE($^3CH_2$)	83771.9	±3.0
IE($^1CH_2$)	80623.8	±5.3
IE(^{2}CH)	85831.0	±6.0
IE(^{4}CH)	79835	±43
IE(C)	90820.38	±0.06
EA(CH_3)	729	±20
EA($^3CH_2$)	5257	±14
EA($^1CH_2$)	8405	±15
EA(^{2}CH)	9798	±18
EA(^{4}CH)	15794	±46
EA(C)	10179.68	±0.30
D_0(CH_4)	36150.6	±2.2
D_0(CH_4^+)	13767.8	±3.2
D_0(CH_3 to $^3CH_2$ + H)	38221.0	±7.9
D_0(CH_3 to $^1CH_2$ + H)	41369.1	±8.6
D_0(CH_3^+)	42623.1	±8.3
D_0(CH_3^- to $^3CH_2$ + H^-)	32867	±21
D_0(CH_3^- to CH_2^- + H)	33692	±24
D_0(CH_3^- to $^1CH_2$ + H^-)	36015	±22
D_0($^3CH_2$ to ^{2}CH + H)	34937.9	±8.5
D_0($^3CH_2$ to ^{4}CH + H)	40934	±44
D_0($^1CH_2$ to ^{2}CH + H)	31789.8	±9.1
D_0($^1CH_2$ to ^{4}CH + H)	37786	±44
D_0(CH_2^+)	36997.0	±8.4
D_0(CH_2^- to $^3CH^-$ + H)	30397	±22
D_0(CH_2^- to ^{2}CH + H^-)	34112	±16
D_0(^{2}CH)	27957.3	±6.0
D_0(^{4}CH)	21962	±43
D_0(CH^+)	32946.7	±0.6
D_0(CH^-)	27576	±18

Conclusions

This work establishes new computational benchmarks for the bond dissociation energy of methylidyne. Extended versions of the HEAT and FPD composite model chemistries, which feature large CCSD(T) calculations with up to 9-ζ basis sets predict the bond dissociation energy of methylidyne, D_0(CH), to be 27954 ± 15 cm^{-1} and 27956 ± 15 cm^{-1}, respectively. An important aspect of these estimates is the correct treatment of the coupling of spin, electronic, and rotational angular momenta in the ground $^2\Pi$ state of CH. Additionally, the CH adiabatic ionization energy, IE(CH), is determined *via* extended HEAT to be 85829 ± 15 cm^{-1}, and the bond dissociation energy of methyliumylidene, D_0(CH^+), as 32946 ± 15 cm^{-1}. In terms of direct experimental determinations, only D_0(CH^+) has a sufficiently accurate empirical value[97] (32946.7 ± 0.6 cm^{-1}), and the extended HEAT calculations reproduce this value to within 2 cm^{-1}. For the bond dissociation energy and the adiabatic ionization energy of methylidyne, the theoretical values reported here may be taken as the newest and most accurate computational benchmarks.

The ATcT thermochemical network has been updated by adjusting the description of coupling of the spin to electronic and rotational angular momenta and vibrational zero-point energies, as appropriate, in previously reported high-level theoretical values. The effect of these changes is to move the ATcT D_0(CH) that was based on unadjusted calculated values from the literature by 10 cm^{-1}. The ATcT TN was subsequently expanded by incorporating the present FPD and extended HEAT computational results, providing the final values D_0(CH) = 27957.3 ± 6.0 cm^{-1}, D_0(CH^+) = 32946.7 ± 0.6 cm^{-1}, and IE(CH) = 85831.0 ± 6.0 cm^{-1}. It is hoped that this work will inspire future experimental determinations of D_0(CH) and IE(CH), as the ATcT paradigm works best when both experimental and theoretical data are available.

Conflicts of interest

There are no conflicts to declare.

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