

The enthalpy of formation of ${}^2\Pi$ CH

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The standard enthalpy of formation, $\Delta_f H^\circ$, of ${}^2\Pi$ CH has been determined at converged levels of *ab initio* electronic structure theory, including high order coupled cluster and full configuration interaction benchmarks. The atomic Gaussian basis sets employed include the (aug)-cc-p(V)XZ family with $X = 3, 4, 5$ and 6 . Extrapolations to the complete one-particle basis set and the full configuration interaction limits, where appropriate, have been performed to reduce remaining computational errors. Additional improvements in the enthalpy of formation of ${}^2\Pi$ CH were achieved by appending the valence-only treatment with core–valence correlation, relativistic effects including spin–orbit correlation, and the diagonal Born–Oppenheimer correction. The recommended values for $\Delta_f H_0^\circ$ and $\Delta_f H_{298}^\circ$ of ${}^2\Pi$ CH are $592.48_{-0.56}^{+0.47}$ kJ mol⁻¹ and $595.93_{-0.56}^{+0.47}$ kJ mol⁻¹, respectively.

1. Introduction

With recent significant advances in electronic structure theory and computer hardware, interest in the re-evaluation of thermodynamic properties, especially standard enthalpies of formation, $\Delta_f H_T^\circ$, of smaller radicals, has increased dramatically [1–9]. As $\Delta_f H_T^\circ$ values are often employed in the calculation of enthalpies of reactions, it is preferable to make enthalpies of formation available as a function of temperature T . The best *ab initio* techniques are capable of producing (temperature dependent) enthalpies of formation with error bars smaller than those characteristic of traditional experimental determinations [10–16]. It must be noted, furthermore, that small experimental uncertainties in $\Delta_f H_0^\circ$ or $\Delta_f H_{298}^\circ$ are sometimes unfounded; for example, in the case of the ${}^2\Pi$ OH radical the widely accepted empirical $\Delta_f H_0^\circ$, based on a spectroscopic approach employing the dissociation energy of OH(A² Σ^+), has been 39.12 ± 0.21 kJ mol⁻¹ [2] and it was recently lowered [2], based on a positive ion cycle approach, to 36.94 ± 0.33 kJ mol⁻¹. The revised value is fully supported by high level *ab initio* electronic structure computations [2, 9].

Converged *ab initio* determination of the enthalpy of formation of ${}^2\Pi$ CH is made simpler by the small size of the system, allowing utilization of full configuration interaction (FCI) techniques. Once $\Delta_f H_0^\circ[\text{CH}({}^2\Pi)]$ is established above any reasonable doubt, it helps to

determine the enthalpy of formation of the CH₂ radical. The latter thermochemical quantity, along with those of OH, CH₂OH, HCCO, and CH₂HCO, is crucially important [17], as it is principally responsible for the determination of the performance of combustion models involving hydrocarbons.

Major thermochemical tables recommend values for the atomization energy $D_{0/e}$ and for $\Delta_f H_T^\circ$ (${}^2\Pi$ CH). The best available value for the equilibrium atomization energy of ${}^2\Pi$ CH is $D_e = 351.0 \pm 1.2$ kJ mol⁻¹ [18]. The rather large uncertainty in the experimental value is connected with the fact that the spectroscopic analysis of predissociation effects of CD by Danielsson *et al.* [18] resulted in $D_e^\circ(\text{CH})$ and $D_e^\circ(\text{CD})$ differing by about 2.2 kJ mol⁻¹. Nevertheless, the value obtained in this way, 350.9 ± 1.2 kJ mol⁻¹, agrees well with another dissociation energy estimate of the same study, 351.1 ± 1.2 kJ mol⁻¹, based on (a) photofragment spectroscopy of CH⁺ resulting in $D_0^\circ(\text{CH}^+) = 393.66 \pm 0.28$ kJ mol⁻¹ [19], and (b) ionization potentials [20] of 1027.0 ± 1.2 kJ mol⁻¹ and 1086.4 kJ mol⁻¹ for CH and C, respectively. The available empirical values, based on critical data evaluation, for $\Delta_f H_{298}^\circ(\text{CH})$ are 594.1 [13], 594.2 [14], 596.4 ± 1.2 [15] and 597.4 kJ mol⁻¹ [10, 16].

The most straightforward way for the converged *ab initio* determination of $\Delta_f H_0^\circ$ of ${}^2\Pi$ CH goes through the determination of the atomization energy of ${}^2\Pi$ CH, although this may not be the best route for larger systems. The best theoretical approach for this study is offered by the focal-point scheme [21, 22]. The calcula-

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tions reported here for the CH radical are by far the most extensive reported to date.

2. Computational approach

Because the correlation-consistent (cc) family of basis sets (aug)-cc-p(C)VXZ (with cardinal number $X = 2(\text{D}), 3(\text{T}), 4(\text{Q}), 5$, and 6) of Dunning and coworkers [23–25] approach the complete basis set limit in a systematic fashion, they were employed in the focal-point basis set extrapolations of the present study. Specifically, the formulas $E^X = E_{\text{limit}} + a \exp(-bX)$ and $E^X = E_{\text{limit}} + cX^{-3}$ were used for the estimation of the HF and correlation energy limits, respectively. Only the best three and two energies available were employed for the exponential and polynomial extrapolations, respectively.

Reference electronic wavefunctions were determined by the single-configuration restricted (open shell) Hartree–Fock (R(O)HF) and unrestricted Hartree–Fock (UHF) methods. Dynamic electron correlation was accounted for by the coupled cluster (CC) method including all single and double (CCSD) [26] and triple excitations (CCSDT) [27]. The CCSD(T) method [28, 29], which estimates the effect of connected triple excitations through a perturbative term [(CT)], was also employed extensively. The full configuration interaction (FCI) computations utilized an ROHF reference wavefunction. For valence focal-point correlation energy computations the $1s$ core orbital of carbon was excluded from the active space. No virtual orbitals were frozen in any of the calculations.

The most recent experimental equilibrium bond distance $r_e/\text{\AA} = 1.119\,786$ [30] was adopted for all electronic structure computations in the valence focal-point analysis and during the auxiliary energy calculations.

Core correlation effects [31, 32] were determined by means of all-electron and frozen-core treatments up to FCI (usually CCSDT) with the (aug)-cc-pCVXZ ($X = 2, 3, 4, 5$, and 6) basis sets.

Relativistic effects [33, 34] were gauged by first-order perturbation theory applied to the one-electron mass–velocity and Darwin terms (MVD1). This relativistic energy correction was augmented with an empirical correction due to spin–orbit interaction.

Computation of the diagonal Born–Oppenheimer (DBOC) correction [35, 36] was performed at the Hartree–Fock level within the formalism of Handy, Yamaguchi and Schaefer [35].

Different versions of the program packages Aces II [37] and PSI [38] were used for the electronic structure computations.

3. Discussion

Tables 1 and 2 summarize the atomization energy results obtained using the focal-point scheme [21, 22] for the valence-only and all-electron treatments, respectively.

In a recent study [39] a simple multiplicative procedure, termed scaled higher order correlation or SHOC, was suggested to estimate higher order correlation (HOC) energies not covered, for example, in CCSD(T) or CCSDT treatments. This procedure, which scales correlation energies and not total energies, utilizes the observation that HOC energy increments show limited basis set dependence, and thus even at the complete basis set limit they may be estimated from explicit small basis set FCI and CCSD(T) or CCSDT calculations. From our extensive computations it became clear that the augmented basis sets are more amenable to this correction. The aug-cc-pVXZ CCSDT

Table 1. Valence focal-point analysis of the atomization energy (in kJ mol^{-1}) of $\text{CH}(\text{}^2\Pi)$.^a

	ROHF	$\delta[\text{CCSD}]$	$\delta[\text{CCSD(T)}]$	$\delta[\text{CCSDT}]$	$\delta[\text{FCI}]$	FCI
aug-cc-pVDZ	233.304	+86.726	+2.715	+0.561	+0.192	323.498
aug-cc-pVTZ	238.839	+102.194	+3.523	+0.381	+0.209	345.147
aug-cc-pVQZ	239.296	+105.889	+3.657	+0.360	+0.213 ^b	349.414 ^b
aug-cc-pV5Z	239.413	+106.930	+3.707	+0.345	+0.218 ^b	350.613 ^b
aug-cc-pV6Z	239.434	+107.355	+3.662	[+0.345]	[+0.218]	[351.015]
Extrapolated ^c	239.438	+107.943	+3.598	[+0.345]	[+0.218]	[351.542]

^a See text for explanation of column headings and basis sets and for details about the extrapolation to the basis set limit for ROHF, $\delta[\text{CCSD}]$ and $\delta[\text{CCSD(T)}]$. Only the results obtained with an ROHF reference wavefunction are included. See text for details concerning the extrapolation procedure employed.

^b Obtained using the SHOC scheme (see text).

^c Results obtained as part of this study with the cc-pVXZ ($X = 4, 5, 6$) basis sets are not presented here. Nevertheless, (i) at the basis set limit the extrapolated cc-pVXZ ($X = 4, 5, 6$) ROHF value differs from that presented in the table by a mere $+0.006 \text{ kJ mol}^{-1}$, and (ii) at the basis set limit the cc-pVXZ ($X = 5, 6$) $\delta[\text{CCSD}]$ increment differs from that presented in the table only by $+0.056 \text{ kJ mol}^{-1}$. Differences from the values presented in this table due to the use of a UHF reference are $-1.28 \text{ kJ mol}^{-1}$ and $+1.23 \text{ kJ mol}^{-1}$ for the extrapolated HF and $\delta[\text{CCSD}]$ cases, respectively. Therefore at correlated levels the ROHF and UHF procedures result in the same limiting values, giving further support to the final dissociation energies given in this study.

Table 2. Focal-point analysis of the core contribution to the atomization energy (in kJ mol^{-1}) of $\text{CH}({}^2\Pi)$.^a

	$\delta[\text{CCSD}]$	$\delta[\text{CCSD(T)}]$	$\delta[\text{CCSDT}]$	$\delta[\text{FCI}]$
cc-pCVDZ	0.498	0.098	0.007	-0.049
aug-cc-pCVDZ	0.663	0.096	0.004	-0.050
cc-pCVTZ	0.419	0.171	0.038	
aug-cc-pCVTZ	0.527	0.172	0.038	
cc-pCVQZ	0.419	0.207	0.054	
aug-cc-pCVQZ	0.431	0.209	0.054	
cc-pCV5Z	0.429	0.215	0.056	
aug-cc-pCV5Z	0.431	0.218		
aug-cc-pCV6Z	0.435	0.218		
Extrapolated	0.439	0.218	0.057	

^a See footnote *a* to table 1.

SHOC scale factors for $\text{C}({}^3\text{P})$ are 1.000212, 1.000189, 1.000200, and 1.000196 for $X = 2, 3, 4,$ and $5,$ respectively. The aug-cc-pV X Z CCSDT SHOC scale factors for $\text{CH}({}^2\Pi)$ are 1.000777 and 1.000720 for $X = 2$ and $3,$ respectively. In line with these values the cc-pVQZ CCSDT SHOC factor is 1.000711. The SHOC factors at the CCSD(T) level are substantially larger: using the largest available basis sets they are 1.005651 and 1.004733 for $\text{CH}({}^2\Pi)$ and $\text{C}({}^3\text{P}),$ respectively. The CCSDT SHOC factors of 1.000720 and 1.000196 were employed for the valence-only treatments of $\text{CH}({}^2\Pi)$ and $\text{C}({}^3\text{P}),$ respectively. Using the best CCSD(T) and CCSDT sets of SHOC factors shows agreement within 0.02 kJ mol^{-1} for the atomization energy of ${}^2\Pi$ CH.

The calculated valence-only atomization energies provide lower limits to the correct result, because extension of the basis set as well as the electron correlation treatment increase the calculated atomization energies. The valence-only complete basis set FCI atomization energy of ${}^2\Pi$ CH is $351.54_{-0.30}^{+0.10} \text{ kJ mol}^{-1},$ where a small $\pm 0.10 \text{ kJ mol}^{-1}$ allowance was made to account for the possible overestimation of the CCSD energy increment.

As seen in table 2, the core contribution to the atomization energy of $\text{CH}({}^2\Pi)$ is rather small: the best estimate is $+0.66 \pm 0.06 \text{ kJ mol}^{-1}$ at the estimated complete basis set FCI limit.

The MVD1 relativistic correction to the atomization energy of ${}^2\Pi$ CH was computed at the HF and CCSD(T) levels using aug-cc-pCV X Z, $X = 2, 3, 4,$ and $5,$ basis sets. The correction is a mere $-0.16 \text{ kJ mol}^{-1},$ obtained at the aug-cc-pCV5Z CCSD(T) level. The correlation contribution included in this value is $+0.04 \text{ kJ mol}^{-1},$ independent of the basis set used. The HF relativistic energy corrections for $\text{C}({}^3\text{P})$ and $\text{CH}({}^2\Pi)$ hardly show convergence with respect to basis set enlargement, but their difference does, as observed repeatedly in [34]. The overall small one-electron relativistic correction and the fact that two-electron relativistic energy

corrections are usually comparable with the electron correlation contribution to the MVD1 energy correction [34] indicate that relativistic corrections beyond MVD1 should have a negligible effect even at the level of precision sought in this study; therefore we set the scalar relativistic correction to $-0.16 \pm 0.04 \text{ kJ mol}^{-1}.$ The next relativistic energy correction considered is due to the spin-orbit effect. Traditional non-relativistic electronic structure calculations yield the weighted average of the available multiplets. To obtain the energy of the lowest one, we used the experimental spin-orbit splitting constants from [40] for the ${}^3\text{P}$ state of carbon and from [30] for CH. The final relativistic correction is $-0.33 \pm 0.06 \text{ kJ mol}^{-1},$ to be added to the computed atomization energy.

The DBOC corrections, in $\text{cm}^{-1},$ computed at the Hartree-Fock level using a medium size TZ2Pf+diff basis set are $+59.7, +365.9,$ and $+441.7$ for $\text{H}({}^2\text{S}),$ $\text{C}({}^3\text{P}),$ and $\text{CH}({}^2\Pi),$ respectively, resulting in an overall DBOC correction to the atomization energy of $-16.2 \text{ cm}^{-1},$ i.e., $-0.19 \text{ kJ mol}^{-1}.$ This small value is still considerably larger than $-0.028 \text{ kJ mol}^{-1},$ the value obtained for the $\text{OH} \rightarrow \text{O} + \text{H}$ dissociation reaction [9] at the CASSCF(7,2)/aug-cc-pVTZ level. Therefore, our DBOC value may be slightly exaggerated, which prompted us to add an asymmetric error bar of -0.05 and $+0.15$ to the computed value.

Collecting all the terms and assuming independent error bars for the different terms, we obtain our best estimate for the equilibrium atomization energy of ${}^2\Pi$ CH as $351.54_{-0.30}^{+0.10} + 0.66_{-0.06}^{+0.06} - 0.33_{-0.06}^{+0.06} - 0.19_{-0.15}^{+0.05} = 351.68_{-0.34}^{+0.13} \text{ kJ mol}^{-1}.$ This value is to be compared with the best experimental equilibrium dissociation energy available [18], $351.0 \pm 1.2 \text{ kJ mol}^{-1}.$

A value for the molecular zero-point energy (ZPE) of ${}^{12}\text{C}^1\text{H},$ $16.941 \text{ kJ mol}^{-1},$ may be taken from the recent high quality experimental work of Zachwieja [30], who determined term values $T_i, i = 1-4,$ for methyldyne.

The ZPE value of Zachwieja compares very well with a high level variational *ab initio* estimate [41] of $16.949 \text{ kJ mol}^{-1}$. Therefore, we estimate that the zero-point energy of methyldine is $16.941 \pm 0.010 \text{ kJ mol}^{-1}$.

In summary, the best theoretical value of this study for D_0 , with a conservative error estimate, is $334.74_{-0.34}^{+0.13} \text{ kJ mol}^{-1}$. The W1 estimate [42] is $335.2 \text{ kJ mol}^{-1}$ with no error bar attached. The value given by Feller and Dixon [7] is $334.7 \pm 0.4 \text{ kJ mol}^{-1}$, where the computational error was probably underestimated. These values, obtained by somewhat different theoretical techniques, suggest that the atomization energy of $^2\Pi \text{ CH}$ is known with the claimed precision. Therefore, we advocate the upward revision of the recommended equilibrium and zero-point corrected dissociation energies of $^2\Pi \text{ CH}$ to $351.7 \text{ kJ mol}^{-1}$ and $334.7 \text{ kJ mol}^{-1}$, respectively.

Calculation of the enthalpy of formation from the atomization energy requires the knowledge of the enthalpy of formation of the atoms H and C in their respective ground states. The relevant data, when available, were taken from [12], and in kJ mol^{-1} are $\Delta_f H_{298}^\circ[\text{C}(\text{}^3\text{P})] = 716.68 \pm 0.45$, $\Delta_f H_{298}^\circ[\text{H}(\text{}^2\text{S})] = 217.998 \pm 0.006$, $H_{298} - H_0[\text{H}] = 6.197 \pm 0.001$, $H_{298} - H_0[\text{H}_2] = 8.468 \pm 0.001$, $H_{298} - H_0[\text{C}_{\text{graphite}}] = 1.050 \pm 0.20$, and $H_{298} - H_0[\text{C}_{\text{gas}}] = 6.536 \pm 0.001$. The resulting 0 K atomic enthalpies of formation are $\Delta_f H_0^\circ[\text{H}(\text{}^2\text{S})] = 216.034 \pm 0.006 \text{ kJ mol}^{-1}$ and $\Delta_f H_0^\circ[\text{C}(\text{}^3\text{P})] = 711.19 \pm 0.45 \text{ kJ mol}^{-1}$. The $H_{298} - H_0$ value for CH was taken from [14] as $8.730 \text{ kJ mol}^{-1}$. Based on these experimental values, the final computational value for $\Delta_f H_0^\circ$ of $^2\Pi \text{ CH}$ is $592.48_{-0.56}^{+0.47} \text{ kJ mol}^{-1}$. This value is somewhat lower and with a lower error limit than the best experimental estimate of $593.0 \pm 1.2 \text{ kJ mol}^{-1}$ [15]. On the other hand, it is significantly higher than the $590.683 \text{ kJ mol}^{-1}$ recommended by JANAF [14] and significantly lower than the $594.0 \text{ kJ mol}^{-1}$ recommended in further databases [10, 16]. The best recommended computational value for $\Delta_f H_{298}^\circ$ is $595.93_{-0.56}^{+0.47} \text{ kJ mol}^{-1}$.

4. Conclusion

We have calculated *ab initio* the equilibrium and zero-point energy corrected dissociation energies of $^2\Pi \text{ CH}$ with recommended values of $351.68_{-0.34}^{+0.13} \text{ kJ mol}^{-1}$ and $334.74_{-0.34}^{+0.13} \text{ kJ mol}^{-1}$, respectively. These results allow the estimation of the standard enthalpy of formation, $\Delta_f H_T^\circ$, of $^2\Pi \text{ CH}$. The results obtained, $592.48_{-0.56}^{+0.47} \text{ kJ mol}^{-1}$ and $595.93_{-0.56}^{+0.47} \text{ kJ mol}^{-1}$ for $\Delta_f H_0^\circ$ and $\Delta_f H_{298}^\circ$, respectively, are somewhat different from the best available empirical results and have smaller error bars. Our final result for the 0 K enthalpy of formation of $^2\Pi \text{ CH}$ shows that we may calculate $\Delta_f H_0^\circ$ for such a small species reliably within about 0.5 kJ mol^{-1} . Further improvement on the error bar of the computed enthalpy

of formation must await a value with much increased precision for the atomic enthalpy of formation of C_{gas} .

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