

## ***Ab initio* post-HF CCSD(T) Calculations for Triplet and Singlet Methylene in Four Consecutive Dunning Basis Sets with Extrapolations to Infinite Limits for Various Molecular Properties**

Alexander Neugebauer<sup>1</sup> and Günter Häfelinger<sup>2,\*</sup>

<sup>1</sup> Saarland University, Pharmaceutical and Medicinal Chemistry, Im Stadtwald, Building 32, D-66123 Saarbruecken, Germany. Tel.: (+49)-681-302-3224; Fax: (+49)-681-302-4386  
e-mail: [a.neugebauer@mx.uni-saarland.de](mailto:a.neugebauer@mx.uni-saarland.de)

<sup>2</sup> University of Tuebingen, Institute of Organic Chemistry, Auf der Morgenstelle 18, D-72076, Tuebingen, Germany. Phone: (+49)-7071-29-72440; Fax: (+49)-7071-29-5080

*Dedicated to Prof. Dr. Marvin Charton, a friend from the CAIC group*

\*Author to whom correspondence should be addressed; e-mail: [guenter.haefelinger@uni-tuebingen.de](mailto:guenter.haefelinger@uni-tuebingen.de)

*Received: 8 October 2004; in revised form: 10 December 2004 / Accepted 10 December 2004 /*

*Published: 31 January 2005*

---

**Abstract :** Stationary points for four geometrically different states of methylene: bent and linear triplet methylene, bent and linear singlet methylene were investigated using the highly reliable post-HF CCSD(T) method. Extrapolations to the CCSD(T) basis set (CBS) limit from Dunning triple to quintuple correlation consistent polarized basis sets were performed for total energies, for the equilibrium CH distances  $r_e(\text{CH})$ , for singlet-triplet separation energies, for energy barriers to linearity and for correlation energies. Post-HF calculations with Dunning basis sets of the literature are presented for comparisons.

**Keywords:** Ab initio CCSD(T) calculations; Extrapolations to Dunning basis set limits of infinity; Geometry of stationary points for lowest triplet and singlet states of methylene; Total energies, singlet-triplet separation energies, barriers to linearity and correlation energies

---

## Introduction

Methylene ( $\text{CH}_2$ ), the parent compound of divalent carbon species, is of great interest in organic chemistry related to its importance in synthesis and to the description and determination of its molecular structure. Due to its small size it is a favoured test case for practically any kind of advanced quantum chemical calculations in respect of its unusual bonding situation in the electronically and geometrically different singlet and triplet states. In the early sixties the molecular structure of singlet and especially triplet methylene ( $\text{CH}_2$ ) was controversially discussed both from experimental and calculational studies as described below.

*Ab initio* calculations with large basis sets and quantum chemistry of a high level of theory have greatly contributed to determine the correct structure of this small molecule. Excellent reviews on the historical aspects related to interplay of experiments and calculations with many references to relevant publications up to 1985 are presented by Shavitt [1], Goddard [2], and Schaefer [3, 4].

Some milestones of these investigations will be mentioned shortly: Foster and Boys [5] predicted in 1960 by an early *ab initio* calculation a bent structure of triplet  $\text{CH}_2$  with a HCH valence angle of  $129^\circ$ , in contrast to an early experimental linear structure determined by Herzberg [6] which was corrected subsequently [7] to the apparent non-linear geometry with an angle around  $136^\circ$ . A highly accurate equilibrium structure of the triplet ground state of  $\text{CH}_2$  was determined experimentally by Bunker and Jensen [8] in 1983 and refined in 1988 [9] leading to highly accurate values of  $r_e(\text{CH}) = 1.0753 \pm 0.0003 \text{ \AA}$  with a valence angle  $\theta_e(\text{HCH})$  of  $133.93 \pm 0.06^\circ$ . The experimental geometry of the lowest singlet state of  $\text{CH}_2$  as determined by Petek et al. [10] in 1989 with less precise values of  $r_e(\text{CH}) = 1.107 \pm 0.002 \text{ \AA}$  and  $\theta_e(\text{HCH}) = 102.4 \pm 0.4^\circ$ .

Quantum chemical models of *ab initio* MO calculations may be classified by the following levels of theory which are treated in detail in the excellent book of Helgaker, Joergensen and Olsen [11]:

- 1) The Hartree-Fock (HF) self-consistent-field (SCF) method uses one Slater determinant of LCAO-MO's describing a single configuration of electrons which may serve as a reference state for most of the following post-HF models.
- 2) Configuration-interaction (CI) theory is based on a linear superposition of Slater determinants describing excitations of electrons from a reference state with variational determination of the expansion coefficients. Truncated configurations may use single (one-electron) excitations (S), double (two-electron) excitations (D) or similarly triple (T) or quadruple (Q) excited configurations. Treatment of all possible excited configurations are termed full CI (FCI).
- 3) The multireference CI (MRCI) method uses several determinants as reference configurations and generates all excitations up to a given level from each reference configuration, i. e. if all single and double excitations are included results the MRSDCI model. Alternatively this may be termed second order CI (SOC) for single and double excitations out of a CASSCF reference function.
- 4) The multiconfigurational self-consistent field (MCSCF) method uses CI determinants which are variationally optimised simultaneously with the expansion coefficients. The MO space may be partitioned into three subspaces containing inactive (doubly occupied), virtual (unoccupied) and active orbitals (with variable occupancies of 0, 1 or 2 electrons). A MCSCF expansion

distributing the active electrons in all possible ways among the active orbitals which is leading to non-integer occupancies is termed complete active space (CAS) method.

- 5) The coupled-cluster (CC) model treats excitations between pair-wise correlated electrons (pair clusters) in a non-linear way via a cluster operator acting on a single-determinantal reference state. The cluster operator is partitioned into classes of all single (S), double (D) or triple (T) excitations, In the CCSD(T) method [12, 13] are contributions from triple excitations estimated by a perturbative treatment. The CC methods account well for dynamical electron correlation.
- 6) Perturbation theory is applied as Møller-Plesset (MP) perturbation of second, third or fourth order (MP2, MP3 or MP4) related to HF SCF as the unperturbed reference state

All of these methods depend critically on the size and quality of applied Gaussian basis sets for one-electron atomic functions.

The convergence to the basis set limit (this means that the total energy will not change if one adds some more Gaussian basis functions) is generally very slow. Basis set series which comprise systematic improvements of the ground state energy or other properties allow an extrapolation based on the asymptotic behaviour of the series with increasing basis set expansion. Examples for such series of basis sets are the correlation-consistent polarized valence basis sets of Dunning [14] and [15] termed cc-pVXZ with zeta exponents from  $X = 2$  to 5 which we use here, or the atomic natural orbital (ANO) basis sets of Almlöf, Taylor and Helgaker [16, 17, 18].

*Ab initio* Hartree-Fock (HF) calculations lead to unreliable results for  $\text{CH}_2$  [1, 4], therefore post-HF methods have to be applied, with some important contributions for energy hypersurfaces listed as follows:

In 1971 whole energy hypersurfaces of seven low-lying triplet and singlet states of  $\text{CH}_2$  were calculated by the group of Schaefer [19] by configuration interaction (CI) methods and extended in 1983 by MCSCF methods with Dunning's cc-pVDZ basis set [14] for the lowest triplet and singlet states of  $\text{CH}_2$  by Alexander *et al.* [20]. Comeau *et al.* [21] report in 1989 for these states MRCI and MCSCF calculations with a full-valence CAS reference space using an atomic-natural (ANO) basis set of quadruple zeta quality. They calculated vibration-rotation energies using the Morse oscillator rigid bender internal dynamics (MORBID) Hamiltonian to obtain improved fitted potential energy surface parameters. Recently CCSD(T)/cc-pVTZ calculations were fitted by three different analytical functions to determine the global potential energy surface of the triplet ground state of methylene [22]. Important post-HF calculations since 1985 for triplet and/or singlet  $\text{CH}_2$  will be mentioned here: Bauschlicher and Taylor [23, 24, 25, 26] performed around 1987 various FCI studies with respect to the size of the triplet-singlet separation energy of  $\text{CH}_2$  with Dunning basis sets [14]. In 1995 and 1997 Dunning *et al.* [27, 28] applied MP2, MP3 and MP4, coupled cluster (CCSD and CCSD(T)) and MRCI CAS methods for the triplet and singlet states of  $\text{CH}_2$  using their valence basis sets from cc-pVDZ up to cc-pVQZ [15] and core-valence basis sets cc-pCVXZ [27]. In 1995 Schaefer *et al.* [4] performed CCSD(T) and frozen-core FCI benchmark calculations for the ground and first excited triplet and singlet states of  $\text{CH}_2$  using a relatively small DZP basis set of Dunning type which was extended by this group in 1998 to the larger TZ2P basis set calculations [29]. The most extensive *ab initio* post-HF calculations reported till now for singlet and triplet  $\text{CH}_2$  but with a fixed geometry using CI methods (CISD, CISDT, CISDTQ up to FCI) and coupled-cluster methods (CCSD, CCSD(T) and CCSDT) with Dunning valence [15] and core-valence [27] basis sets cc-pVXZ and cc-pCVXZ for  $X =$

2 to 6 have been presented in 2003 by Császár *et al.* [30], when our calculations had already been finished independently.

In our work we concentrate on CCSD(T) calculations with Dunning's cc-pVXZ basis set series [15] from double-zeta ( $X = 2$ ) to quintuple-zeta ( $X = 5$ ) quality which all include appropriate polarization functions on carbon and hydrogen and we will present comparisons to calculated and experimental literature data.

As aim of our publication we present in the first part frozen-core CCSD(T) optimisations to investigate the geometry and energy of stationary points of the bent triplet  $^3B_1$  ground state of  $CH_2$  (**1**), the linear triplet state of  $CH_2$  (**2**), the bent singlet  $^1A_1$  ground state of  $CH_2$  (**3**) and the linear singlet state of  $CH_2$  (**4**) by the CCSD(T) procedure using four of the already mentioned consecutive Dunning [15] cc-pVXZ basis sets.

From these calculations as an extrapolation to the basis set limit an empirical exponential function of the general form of eqn. 1:

$$P(X) = P(\infty) + a \cdot e^{-b \cdot X} \quad (1)$$

can be used, where  $P(X)$  is an energy or property dependent on the basis set expansion  $X$  and  $P(\infty)$  is the predicted value in the corresponding basis set limit (BS limit). Such extrapolations have been applied first for energies by Feller in 1992 [31] and used by Dunning [27] and by Császár [30]. Test extrapolations with alternatively polynomial or potential functions lead to similar results. Here exponential extrapolations are obtained from cc-pVTZ, cc-pVQZ and cc-pV5Z valence basis sets [15], denoted as TQ5-limit for frozen-core CCSD(T) calculations.

Exponential extrapolations for three consecutive basis sets to the infinite BS limit via eqn. 1 for the four different  $CH_2$  **1** to **4** species have been carried out as usual for total energies, but further concerning equilibrium  $r_e$  CH distances, singlet-triplet separation energies ( $T_e$ ), energy barriers to linearity and correlation energies. A further additional estimation from the best calculated to a predicted experimental equilibrium  $r_e$  CH distance as described in ref. [32] has been performed.

## Calculational Procedure

Molecular geometries and energies of  $CH_2$  were determined for stationary points of  $CH_2$  **1** to **4** by ab initio post-HF MO frozen-core optimisations using the CCSD(T) method as very successful approximation for the principally unknown accurate many-electron wave function [11] and alternatively as lower approximation the density functional (DFT) [33] Becke 3-parameter Lee-Yang-Parr [34] (B3LYP) hybrid method. Four consecutive correlation consistent (cc) polarized valence basis sets of Dunning [15] (which are abbreviated by cc-pVXZ in relation to the number of zeta-exponents, where  $X$  indicates  $D = 2$ ,  $T = 3$ ,  $Q = 4$  and  $5$  zeta exponent splittings) were applied for the valence electron frozen-core CCSD(T) calculations. The number of contracted Gaussian basis functions for  $CH_2$  are: cc-pVDZ = 24, cc-pVTZ = 58, cc-pVQZ = 115 and cc-pV5Z = 201.

All calculations were performed with Pople's Gaussian 98 program system (Rev. A.7) [35] using the unrestricted procedure for the triplet states of methylene. The status of stationary points was checked by frequency calculations. The DFT B3LYP calculations were performed in the cc-pVTZ basis set and the 'fine' integration grid of Gaussian 98 was used for enhanced accuracy. These results are not presented here but may be obtained from the authors.

## Results and Discussion

## Total Energies

In Table 1 total energies from various frozen-core post-HF calculations from the literature with Dunning valence cc-p-VXZ basis sets [15] for triplet CH<sub>2</sub> in forms **1** and **2** are collected in comparison to our CCSD(T) results together with exponential extrapolations via eqn. 1 to estimate infinite basis set (CBS) limits for the final energies obtainable with the CCSD(T) method. Corresponding values for singlet CH<sub>2</sub> in forms **3** and **4** are presented in Table 2.

**Table 1.** Post-HF frozen-core calculations of total energies [Hartree] with Dunning basis sets for triplet methylenes **1** and **2**. Own CCSD(T) calculations with exponential TQ5 CBS limits via eqn. 1 and literature data for different methods.

Molecule	Method	Basis set	E <sup>a</sup> this work	E <sup>b</sup> [30]	E <sup>c</sup> [28]	E	Ref.
<sup>3</sup> B <sub>1</sub> CH <sub>2</sub> <b>1</b> bent triplet GS	CCSD(T)	cc-pVDZ	-39.041816	-39.041248	-39.041564	-39.046371 <sup>c</sup>	[4]
		cc-pVTZ	-39.077854	-39.077802	-39.077501	-39.066184 <sup>f</sup>	[29]
		cc-pVTZ				-39.094104	[22]
	CCSDT	cc-pVQZ	-39.087331	-39.087285	-39.086958		
		cc-pV5Z	-39.090075	-39.090029	-39.089024 <sup>d</sup>		
		cc-pV6Z	-	-39.090903	-		
			<b>CBS limit</b>	<b>-39.0912</b>	<b>-39.092197<sup>j</sup></b>	<b>-39.09174</b>	
	FCI	cc-pVDZ			-39.041670		
		ANO			-39.078279		
		cc-pVQZ			-39.087741		
	FCI	cc-pVDZ			-39.041695		-39.046816 <sup>c</sup> [4]
		ANO					-39.046260 [23]
	CISD	cc-pVTZ			-39.078346		-39.066738 <sup>f</sup> [29]
		cc-pVDZ					-39.036887 -39.045381 [52]
							-39.070465 -39.080444 [52]
							-39.079271
							-39.081170 <sup>d</sup>
	MP4	cc-pVDZ					-39.040477
		cc-pVTZ					-39.076541
		cc-pVQZ					-39.085976
cc-pV5Z/QZ						-39.088060 <sup>d</sup>	
CAS+1+2	cc-pVDZ					-39.040273	
	cc-pVTZ					-39.074544	
	cc-pVQZ					-39.083477	
	cc-pV5Z/QZ					-39.085397 <sup>d</sup>	
CMRCI <sup>g</sup>	cc-pCVDZ					-39.041579 [27]	
	cc-pCVTZ					-39.075452 [27]	
	cc-pCVQZ					-39.083886 [27]	
	cc-pCV5Z					-39.086206 [27]	
		<b>CBS limit</b>				<b>-39.08796</b> [27]	
MCI CAS	cc-pCVTZ					-39.07989 [49]	
MRCI IS <sup>h</sup>	ANO QZ					-39.083084 [21]	
MRCI SO <sup>i</sup>	ANO QZ					-39.083222 [21]	
MR SOCI	ANO					-39.084972 [25]	

Table 1. Cont.

Molecule	Method	Basis set	E <sup>a</sup> this work	E <sup>b</sup> [30]	E <sup>c</sup> [28]	E	Ref.
<sup>3</sup> Σ <sup>-</sup> CH <sub>2</sub> 2 Linear	CCSD(T)	cc-pVDZ	-39.030906				
		cc-pVTZ	-39.068449			MCI CAS: -39.07895	[49]
		cc-pVQZ	-39.078196				
		cc-pV5Z	-39.081045				
		<b>C BS limit</b>	<b>-39.0822</b>				

Footnotes to Table 1:

- a) CCSD(T) calculations for optimised geometries (see Table 3), this work.
- b) CCSD(T) calculations for constant geometries:  $r_e$  (CH) = 1.07598 Å,  $\theta_e$  (HCH) = 133.848°, ref. [30].
- c) CCSD(T) calculations for optimised geometries (see Table 3), ref. [28].
- d) The Dunning cc-pV5Z/QZ basis set is of type 5Z for C and QZ for H [28].
- e) DZP basis set used in ref. [4].
- f) TZ2P basis set used in ref. [29].
- g) Contracted MRCI CAS CI [27].
- h) MRCI with full CAS interacting space (IS). [21].
- i) MRCI with full second order (SO) CI [21].
- j) Q67 CBS limit.

Due to the quantum mechanical variation principle [11, 36, 37] are these *ab initio* energies an upper limit for the usually unknown true experimental energies. Thus this value is an indication of the quality of the calculations with respect to applied procedures and basis sets.

We concentrate first on the CCSD(T) total energies in Tables 1 and 2. Such calculations by Dunning *et al.* [28] and our results use the same basis sets DZ to QZ, but the 5Z basis sets are different. Both calculations are based on optimised geometries (shown in Tables 3 to 5) and therefore should be identical. The notable differences in energies by about 0.35 mHartree (0.22 kcal/mol) may be due to the applied different computer programs (MOLPRO in ref. [28] and G 98 by us) and lead to different geometries (see Tables 3 and 5). The CCSD(T) calculations of ref. [30] are based on fixed molecular geometries derived from aug-cc-pCVQZ optimisations of **1** and **3** which are very close to experimental geometries. For TZ to 5Z calculations is the difference from [30] values to our energies smaller than above by one order of magnitude. (The presented energies are taken from the supplementary material of ref. [30].)

Three independent extrapolations to the CBS limit lead to CCSD(T) values between -39.0912 and -39.092197 Hartree for **1**, the largest numbers presented in Table 1, except the energy of -39.09404 quoted in ref. [22] which must be erroneous. The extension to the more elaborate CCSDT method with inclusion of all triplet excitations taken from ref. [30] shows only a small improvement by about 0.45 mHartree for the cc-pVXZ data for X = 2 to 4. Comparison to the immense extensive full FCI values (i.e. 560 034 determinants with cc-pVDZ in [30]) which are available only for DZ and TZ basis sets also are better than corresponding CCSD(T) data by only 0.447 and 0.544 mHartree for DZ and TZ, respectively. Selecting a higher Dunning basis set in the CCSD(T) method leads to a larger improvement in energy. This shows the superior behaviour of the CCSD(T) method with respect to energies calculated in all the other post-HF procedures shown in Tables 1 and 2 which are based mainly on calculations of Dunning's group, ref. [27] and [28]. (All energies in ref. [27] are misprinted too low by 2 Hartree.)

**Table 2.** Post-HF frozen-core calculations of total energies [Hartree] with Dunning basis sets for singlet methylenes **3** and **4**. Own CCSD(T) calculations with exponential TQ5 CBS limits via eqn. 1 and literature data for different methods.

Molecule	Method	Basis set	E <sup>a</sup> this work	E <sup>b</sup> [30]	E <sup>c</sup> [27]	E	Ref.
<sup>1</sup> A <sub>1</sub> CH <sub>2</sub> <b>3</b> bent singlet GS	CCSD(T)	cc-pVDZ	-39.022584	-39.022029	-39.024154	-39.025791 <sup>e</sup>	[4]
		cc-pVTZ	-39.061384	-39.061367	-39.062456	-39.048005 <sup>f</sup>	[29]
		cc-pVQZ	-39.071913	-39.071909	-39.072413		
		cc-pV5Z	-39.075039	-39.075037	-39.075244		
		cc-pV6Z	-	-39.076081 <sup>j</sup>	-		
		<b>CBS limit</b>	<b>-39.0764</b>	<b>-39.076408<sup>k</sup></b>	<b>-39.07733</b>		
	CCSDT	cc-pVDZ			-39.022748		
		cc-pVTZ			-39.062180		
		cc-pVQZ			-39.072695		
	FCI	cc-pVDZ	-		-39.022937	-39.026635 <sup>e</sup>	[4]
		ANO				-39.027183	[24]
	FCI	cc-pVTZ			-39.062405	-39.048984 <sup>f</sup>	[29]
	CMRCI <sup>g</sup>	cc-pCVDZ				-39.023177	[27]
		cc-pCVTZ				-39.059919	[27]
		cc-pCVQZ				-39.069396	[27]
		cc-pCV5Z				-39.072067	[27]
		<b>CBS limit</b>			<b>-37.07405</b>	[27]	
MRCI IS <sup>h</sup>	ANO QZ				-39.068284	[21]	
MRCI SO <sup>i</sup>	ANO QZ				-39.068284	[21]	
SOCI	ANO				-39.070250	[25]	
<hr/>							
<sup>1</sup> Δ <sub>g</sub> CH <sub>2</sub> <b>4</b> linear singlet	CCSD(T)	cc-pVDZ	-38.967818				
		cc-pVTZ	-39.010679				
		cc-pVQZ	-39.022215				
		cc-pV5Z	-39.025820				
		<b>CBS limit</b>	<b>-39.0275</b>				

Footnotes to Table 2:

- a) CCSD(T) calculations for optimised geometries (see Table 4), this work.  
 b) CCSD(T) calculations for constant geometries:  $r_c$  (CH) = 1.106901 Å,  $\theta_c$  (HCH) = 102.137°, ref. [30].  
 c) CCSD(T) calculations for optimised geometries (see Table 4). Core-valence basis sets cc-pCVXZ (X = 2 to 5) derived and used in ref. [27]. Energies are misprinted by 2 Hartree.  
 e) DZP basis set used in ref. [4].  
 f) TZ2P basis set used in ref. [29].  
 g) Contracted MRCI using full valence and CAS CI [27].  
 h) MRCI with full CAS interacting space (IS). [21].  
 i) MRCI with full second order (SO) CI [21].  
 j) CCSD(T)/aug-cc-pCV6Z calculation for constant geometries shown in Table 4, ref. [30].  
 k) Largest used basis set of type: aug-cc-pCV6Z with 533 contracted Gaussians [30].

Total energies for the singlet forms **3** and **4** which are presented in Table 2 show a similar behaviour as those in Table 1. Our CCSD(T) energies of **3** are lower than those of ref. [30], decreasing from 0.56 mHartree for DZ to nearly full agreement of 0.002 mHartree for 5Z. Dunning's energy

values cannot be compared because of use of the larger core-valence correlated cc-pVCXZ basis sets [27]. The estimated CBS limit is -39.0764 Hartree for **3** from our calculation and -39.0773 Hartree from [27]. The largest CCSD(T) energy calculated in [30] is -39.076408 Hartree close to our CBS limit. Differences from explicit CCSDT versus lower CCSD(T) calculations [30] are around 0.8 mHartree corresponding to 0.5 kcal/mol. Deviations between FCI and CCSD(T) energies are only 0.091 mHartree and 1.04 mHartree for DZ and TZ basis sets [30], respectively. The CMRCI CBS limit [27] is with -37.07405 Hartree slightly smaller than the above mentioned estimated CCSD(T) limits.

For **2** and **4**, the linear forms of CH<sub>2</sub>, are only few reliable post-HF calculations available. Therefore our energies stay in Tables 1 and 2 without discussion but they will be used later for calculations of barriers to linearity.

### Core-Valence Correlation

A further improved treatment for highly accurate energies needs to consider core-valence correlation of all electrons with correspondingly designed core-valence basis sets [27]. This was studied numerically in ref. [26], [27] and [30]. In this case for **1** a CCSD(T) extrapolated CBS limit of -39.14803 Hartree is reached. An all electron core-valence CMRI+Q calculation [27] with the Davidson correction (Q) for CI truncation [38] leads to a CBS limit value of -39.14832 Hartree, the absolutely lowest energy without relativistic effects known for **1**.

### Equilibrium CH Bond Lengths

The CH bond lengths of molecular states **1** to **4** were optimised via gradient methods at the CCSD(T) level in the frozen-core approximation for each of the four Dunning valence basis sets with numerical  $r_e(\text{CH})$  distances presented in Tables 3 and 4 in comparison to literature data and experimental values which are available for **1**, **2** and **3**. The optimised CH distances decrease with each expansion step of the wave functions. Therefore the exponential extrapolation via eqn. 1 could also be applied successfully for prediction of CH distances defining the CBS limit of the CCSD(T) method. The three CBS limit estimations for **1** in Table 3 are rather close around 1.077 Å but still off the experimental value of  $(1.0753 \pm 0.0003)$  Å.

In ref. [32] we studied the capability of the CCSD(T) CBS limit expansion to predict numerically experimental  $r_e$  distances in bonds of carbon to H, C, N and O and derived eqn. 2:

$$r_e^{\text{exp}} = r(\text{CCSD(T)/CBS}) - 0.0018 \text{ \AA} \quad (2)$$

with an estimated standard deviation of  $\pm 0.0005$  Å as a linear correction for all of the mentioned bonds. For the ground state triplet methylene CH distance of **1** this correction leads to a predicted distance of 1.07526 Å now in perfect agreement to the experimental value listed above. For the linear state **2** is this via eqn. 2 predicted distance 1.0645 Å also in the error limit in agreement to the experimental determination of  $1.060 \pm 0.005$  Å.

For the singlet state CH distance of **3** in Table 4 is our via eqn. 2 predicted CCSD(T) value 1.1059 Å, more distant to the experimental value of  $(1.1070 \pm 0.002)$  Å than the CBS limit value of 1.1077 Å but both are in the quoted experimental error limit. The calculated distance in [30] is with 1.1069 Å noticeable very close to the experimental distance.



**Table 3.** Frozen-core by CCSD(T) and other post-HF methods calculated equilibrium distances  $r_e(\text{C-H})$  [Å] of triplet methylenes **1** and **2** in comparison to experimental and literature distances.

Molecule	Method	Basis Set	$r_e(\text{C-H})^a$	$r_e(\text{C-H})^b$	$r_e(\text{C-H})^c$	$r_e(\text{C-H})$	Ref.
<sup>3</sup> B <sub>1</sub> CH <sub>2</sub> <b>1</b> bent triplet GS	CCSD(T)	cc-pVDZ	1.0957	1.0955	1.0947	1.0875 <sup>e</sup>	[4]
		cc-pVTZ	1.0785	1.0783	1.0782	1.0772 <sup>f</sup>	[29]
		cc-pVQZ	1.0773	1.0771	1.0771	1.07793	[21]
		cc-pV5Z	1.0771	1.0772 <sup>d</sup>	1.0767	1.07114	[22]
		ANO				1.082	[23]
	eqn. 1	<b>CBS limit</b>	<b>1.07706</b>		<b>1.0767</b>	1.079	[25]
	eqn. 2	Prediction	<b>1.07526</b>			1.07598 <sup>g</sup>	[30]
	experiment					1.0748 ± 0.0004	[8]
	experiment					<b>1.0753 ± 0.0003</b>	[9]
		CMRCI	cc-pCVDZ			1.0951	[27]
			cc-pCVTZ			1.0784	
			cc-pCVQZ			1.0773	
			cc-pCV5Z			1.0769	
			<b>CBS limit</b>			<b>1.0769</b>	
		CISD	cc-pVDZ		1.0932		
		cc-pVTZ		1.0758			
		cc-pVQZ		1.0744			
		cc-pV5Z/QZ		1.0744			
	MP4	cc-pVDZ		1.9044			
		cc-pVTZ		1.0774			
		cc-pVQZ		1.0762			
		cc-pV5Z/QZ		1.0762			
	CAS+1+2	cc-pVDZ		1.0959			
		cc-pVTZ		1.0786			
		cc-pVQZ		1.0773			
		cc-pV5Z/QZ		1.0773			
<sup>3</sup> Σ <sup>-</sup> CH <sub>2</sub> <b>2</b> Linear Triplet	CCSD(T)	cc-pVDZ	1.0837				
		cc-pVTZ	1.0676			MCI CAS: 1.068	[49]
		cc-pVQZ	1.0665				
		cc-pV5Z	1.0663				
	eqn. 1	<b>CBS limit</b>	<b>1.0663</b>				
	eqn. 2	Prediction	<b>1.0645</b>				
experiment					<b>1.060 ± 0.005</b>	[8]	

Footnotes to Table 3:

a) This work.

b) Ref. [28]

c) Ref. [27] with core-valence basis sets: cc-pCVXZ (X = 2 to 5).

d) cc-pV5/QZ basis set in ref. [28].

e) DZP basis set used in ref. [4].

f) TZ2P basis set used in ref. [29].

g) Contracted MRCI using full valence and CAS CI [27].

For the linear structure **4** of CH<sub>2</sub> is no experimental value available. The CH distance of the 5Z calculation and the extrapolation to the CBS limit are the same within four digits (as in the case of **2**) and application of eqn. 2 reduces these values by 0.0018 Å.

**Table 4.** Frozen-core by CCSD(T) and other post-HF methods calculated equilibrium distances  $r_e(\text{C-H})$  [Å] of singlet methylenes **3** and **4** in comparison to experimental and literature distances.

Molecule	Method	Basis Set	$r_e(\text{C-H})^a$	$r_e(\text{C-H})^b$	$r_e(\text{C-H})$	Ref.
<sup>1</sup> A <sub>1</sub> CH <sub>2</sub> <b>3</b> Bent Singlet GS		cc-pVDZ	1.1291	1.1286	1.1199 <sup>e</sup>	[4]
		cc-pVTZ	1.1105	1.1103	1.1089 <sup>f</sup>	[29]
		cc-pVQZ	1.1086	1.1086	1.10863	[21]
		cc-pV5Z	1.1080	1.1080	1.117	[23]
					1.112	[26]
					1.110	[25]
					1.10691	[30]
	eqn. 1	<b>CBS limit</b>	<b>1.1077</b>	<b>1.1079</b>		
	eqn. 2	Prediction	<b>1.1059</b>			
	experiment				1.1112	[9]
experiment				<b>1.1070 ± 0.002</b>	[10]	
CMRCI <sup>g</sup>	cc-pCVDZ		1.1290			[27]
	cc-pCVTZ		1.1107			
	cc-pCVQZ		1.1088			
	cc-pCV5Z		1.1083			
	<b>CBS limit</b>		<b>1.1081</b>			
<sup>1</sup> Δ <sub>g</sub> CH <sub>2</sub> <b>4</b> Linear Singlet	cc-pVDZ		1.0789			
	cc-pVTZ		1.0645			
	cc-pVQZ		1.0640			
	cc-pV5Z		1.0640			
	eqn. 1	<b>CBS limit</b>	<b>1.0640</b>			
	eqn. 2	Prediction	<b>1.0622</b>		Experiment: 1.070	[51]

Footnotes to Table 4:

a) This work.

b) Ref. [27]

c) Ref. [28] with cc-pCVXZ (X = 2 to 5) basis set.

e) DZP basis set used in ref. [4].

f) TZ2P basis set used in ref. [29].

g) Contracted MRCI using full valence and CAS CI [27].

### HCH Valence Angles

CCSD(T) optimised HCH valence angles of the bent molecular states **1** and **3** are shown in Table 5 in comparison to experimental angles and other reliable calculations.

The calculated angles increase with enlargement of the basis sets. But our CBS extrapolation via eqn. 1 could not be applied for the equilibrium bond angles due to a decrease of our calculated 5Z angle which is not occurring in the calculations of ref. [27] and [28]. This estimated CBS limit for **1**

with  $133.6^\circ$  is off the experimental angle of  $(133.93 \pm 0.01)^\circ$ , but again the optimised angle of ref. [30] is with  $133.85^\circ$  closest to experiment.

For **3** is the estimated CBS limit angle  $102.08^\circ$  [27] and that optimised in [30] is  $102.14^\circ$ , both in the error limit equal to the experimental angle of  $(102.4 \pm 0.04)^\circ$ . Our 5Z angle with  $101.93^\circ$  is again lower than the QZ angle.

**Table 5.** Calculated CCSD(T) and other equilibrium bond angles  $\theta_e$  (HCH) [ $^\circ$ ] of bent methylenes **1** and **3** in comparison to experimental and literature values.

Molecule	Method	Basis Set	$\theta_e(\text{HCH})^{\text{a}}$	$\theta_e(\text{HCH})^{\text{b}}$	$\theta_e(\text{HCH})^{\text{c}}$	$\theta_e(\text{HCH})^{\text{d}}$	Ref.
$^3\text{B}_1$ CH <sub>2</sub> <b>1</b> Bent Triplet GS	CCSD(T)	cc-pVDZ	132.198	132.10	132.13	132.15	[4]
		cc-pVTZ	133.565	133.33	133.33	133.29	[29]
		cc-pVQZ	133.648	133.51	133.51	132.900	[21]
		cc-pV5Z	133.539	133.57	133.56	134.127	[22]
						132.4	[23]
						133.6	[25]
						132.7	[26]
		<b>CBS limit</b>	–		<b>133.59</b>	133.848	[30]
		experiment				133.84±0.05	[8]
		experiment				<b>133.93±0.01</b>	[9]
$^1\text{A}_1$ CH <sub>2</sub> <b>3</b> Bent GS	CCSD(T)	cc-pVDZ	100.542		100.54	101.28	[4]
		cc-pVTZ	101.617		101.63	101.72	[29]
		cc-pVQZ	101.929		101.90	102.137	[30]
		cc-pV5Z	101.914		102.01		
		<b>CBS limit</b>	–		<b>102.05</b>		
	CMRCI <sup>g</sup>	cc-pCVDZ			100.54		
		cc-pCVTZ			101.63		
		cc-pCVQZ			101.90		
		cc-pCV5Z			102.01		
		<b>CBS limit</b>			<b>102.08</b>		
	experiment				101.95	[9]	
	experiment				<b>102.4 ± 0.4</b>	[10]	

Footnotes to Table 5:

- This work.
- Ref. [28].
- Ref. [27] with cc-pCVXZ (X = 2 to 5) basis set.
- DZP basis set used in ref. [4].
- TZ2P basis set used in ref. [29].
- Contracted MRCI using full valence and CAS CI [27].

## Singlet-Triplet Energy Gap

Experimental and calculated energies of the singlet-triplet energy gap (T) of CH<sub>2</sub> up to 1985 are reviewed in ref. [1] with listing of experimental T<sub>0</sub> values (related to the zero vibrational levels of the states **3** and **1**) between 2 to 20 kcal/mol and calculated T<sub>e</sub> energies (which refer to the minima **1** and **3** of the potential energy hypersurface) between 10 and 30 kcal/mol. Compilations of later publications 1997 are presented in ref [4] and [29]. As direct experimental determination [39] is the energetic difference between the singlet state **3** and the triplet state **1** observable from laser photo-detachment spectroscopy of the radical anion CH<sub>2</sub><sup>-</sup> which leads by removal of one electron simultaneously to transitions between various vibration-rotation levels of the triplet or the singlet states of CH<sub>2</sub>. This experiment led to a value of (19.5 ± 0.7) kcal/mol for the energy difference T<sub>0</sub>, close to 22.2 kcal/mol from an early ab initio CI calculation [19].

**Table 6.** Adiabatic singlet–triplet separation energies (T<sub>e</sub>) [kcal/mol] based on data of Tables 1 and 2, referring to minima of potential energy curves without vibrational corrections (1 Hartree = 627.5095 kcal/mol).

cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	cc-pV6Z	Δ CBS <sup>a</sup>	Method <sup>b</sup>	Ref.
12.068	10.335	9.675	9.435	-	<b>9.287</b>	CCSD(T) VE <sup>c</sup>	
12.060	10.313	9.649	9.408	9.301	(9.299) <sup>d</sup>	CCSD(T) VE <sup>e,f</sup>	[30]
12.019	10.527	9.998	9.799	9.661	-	CCSD(T) AE <sup>e,f</sup>	[30]
11.791	10.054	9.408	9.184	-	9.042	CCSD(T) VE <sup>c</sup>	[27]
11.862	10.330	9.792	9.590	-	9.475	CCSD(T) AE <sup>c</sup>	[27]
11.547	9.747	9.093	9.661	8.872	8.729	CMRI VE <sup>e</sup>	[27]
11.652	10.051	9.502	9.307	-	9.193	CMRI AE <sup>e</sup>	[27]
11.496	9.620	8.931	8.699	-	8.553	CMRI+Q VE <sup>e,f</sup>	[27]
11.590	9.901	9.315	9.106	-	8.980	CMRI+Q AE <sup>e,f</sup>	[27]
11.771	10.003					FCI VE <sup>e,f</sup>	[30]
11.729						FCI AE <sup>e,f</sup>	[30]
12.664 [4]	11.141 [29]					FCI VE	
11.97 [23]						FCI VE	[23]
9.287 (IS)	9.373 (SO)					MRCI VE <sup>g</sup>	[21]
9.592 (IS)	9.740 (SO)					MRCI AE <sup>g</sup>	[21]
9.238 SOCI	9.111 (SO+Q)					MRCI VE <sup>g</sup>	[25]
10.608						MCPF AE <sup>g</sup>	[26]
	9.436					CISD	[52]

Experimental determinations of T<sub>e</sub><sup>exp</sup> [kcal/mol]:

- 1) 8.56 ± 0.09 [44]      2) 9.292 ± 0.57 [45]      3) 9.281 ± 0.086 [46]  
 4) **9.215 ± 0.0036** [9]      5) **9.032 ± 0.057** [47]

Footnotes to Table 6:

- a) Difference of CBS limit values.
- b) VE = valence electron correlation, frozen-core. AE = all electron core-valence correlation.
- c) CCSD(T) calculations for optimised geometries, this work.
- d) CBS limit from eqn. 1.
- e) Core-valence basis set: cc-p-CVXZ defined in ref. [27].
- f) CCSD(T) calculations for constant geometries shown in Tables 1 to 4 [30].
- g) ANO basis sets.

That mentioned experiment is a historical important example of the controversial and fruitful interplay between computational and experimental chemistry which is nicely described in ref. [2]. The experimental value of  $T_0$  was in contrast to other ab initio calculations leading to  $T_e = 11.5$  kcal/mol [40] and 13 kcal/mol [41]. This discrepancy was interpreted due to accidentally observed experimental hot bands [42] resulting in a reassignment for  $T_0$  of  $(8.99 \pm 1.15)$  kcal/mol which could be verified later by different experiments [43] leading now to  $T_0 = 9.6$  kcal/mol. An other accurate experimental  $T_0$  energy of  $(9.05 \pm 0.06)$  kcal/mol was measured by McKellar et al. [44] by far-infrared laser magnetic resonance. This is in perfect agreement to a recently calculated  $T_0$  value of 9.025 kcal/mol [52].

In Table 6 we show the basis set and method dependence of calculated  $T_e$  values derived as difference between the total energies of the minima **3** and **1** presented in Tables 2 and 1 and some additional references [45], [46] and [47].

Our CCSD(T) calculated  $T_e$  energies follow again an exponential trend and thus the extrapolation to the CBS limit via eqn. 1 is possible. This CBS (TQ5) limit is 9.299 kcal/mol, somewhat larger than the 9.287 kcal/mol obtained as the difference of the CBS limit values of Table 1 and 2.

Experimental  $T_e$  energies must be derived from  $T_0$  by adjustment to the potential energy curves. This can be done by different approximations. Therefore several experimental  $T_e$  energies are shown in Table 6. Most reliable experimental energies are  $(9.215 \pm 0.004)$  kcal/mol [9] and  $(9.032 \pm 0.057)$  kcal/mol [47] which fit the range of the calculated CCSD(T)  $\Delta$ CBS limit energies between 9.04 and 9.48 kcal/mol.

All  $T_e$  energies of Table 6 decrease with increase of Dunning basis sets: from about 12 kcal/mol for DZ calculations to approximately 10 kcal/mol for TZ, 9.6 for QZ, 9.4 for 5Z and 9.3 kcal/mol for 6Z CCSD(T) calculations.

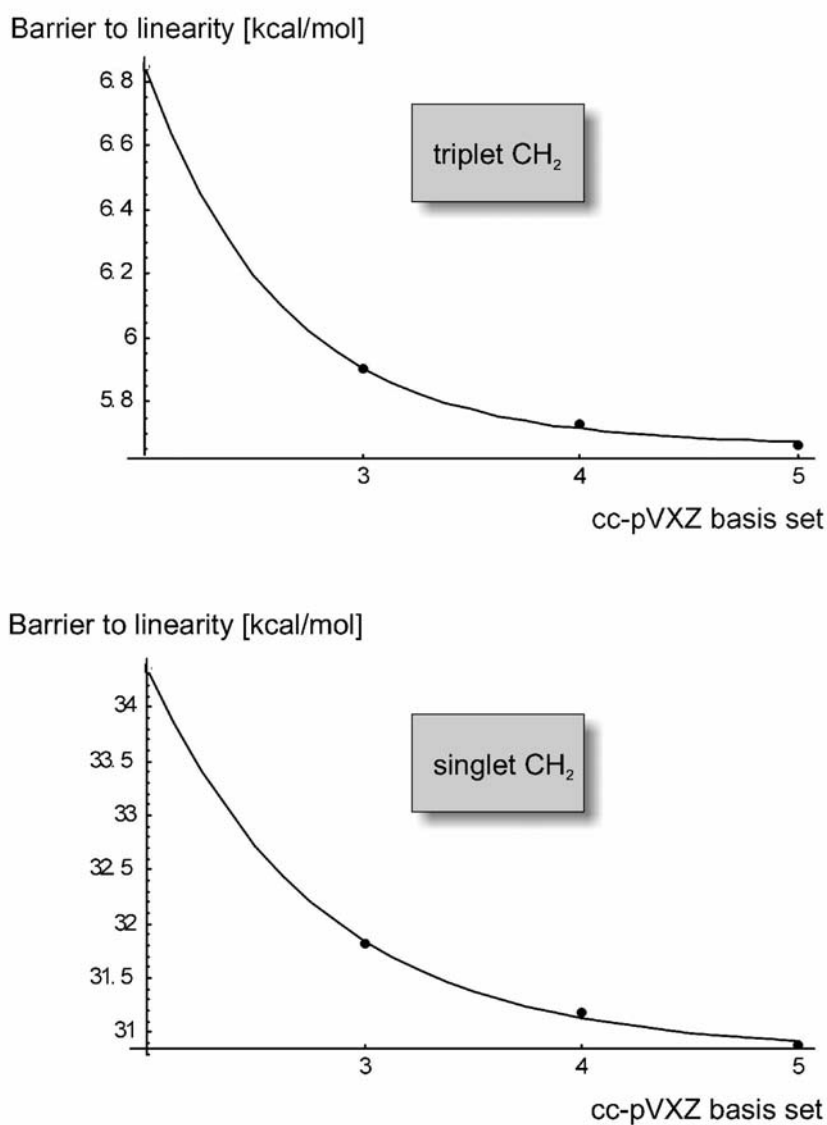
Additional data in Table 6 allow a comparison of valence electron (VE) frozen-core calculations with all electron (AE) core-valence calculations, which use corresponding different Dunning basis sets (cc-p-CVXZ versus cc-p-CVXZ [27]). Mostly are the AE  $T_e$  energies larger than those of VE calculations.

The few available full CI (FCI) DZ and TZ based  $T_e$  energies are in the range of 10 to 12.7 kcal/mol, but slightly lower than the corresponding CCSD(T) values. The elaborate ANO calculations [21] and [25] lead to values in the interval of 9.11 to 9.74 kcal/mol. The numbers presented in Table 6 show clearly that large basis sets (at least QZ) are necessary to reach the range of experimental  $T_e$  determinations.

*Barriers to Linearity*

The total energies of Tables 1 and 2 allow the study of the basis set dependence of the barrier to linearity ( $\Delta E_{BL}$ ) as the difference of energies between the linear and bent conformations of the triplet states (**1** versus **2**) and singlet states (**3** versus **4**). These barriers to linearity have been determined rather seldom by calculations [48], [49] and experimentally [50], [51] and [52] with values shown in Table 7 in comparison to our calculations.

**Figure 1.** Exponential behaviour of barriers to linearity for the cc-pVXZ (X = 2 - 5) basis set expansion. Above: triplet CH<sub>2</sub>, below: singlet CH<sub>2</sub>



Again an exponential extrapolation via eqn. 1 to the CBS limit is possible which is depicted in Figure 1. The CBS limit barrier of the triplet state between **1** and **2** is with 5.623 kcal/mol rather small, in good agreement to the experimental value of 5.48 kcal/mol [8]. The derived CBS limit barrier for

the singlet state is with 30.842 kcal/mol substantially higher but in disagreement to an experimental value around 24.6 kcal/mol.

**Table 7.** Barriers to linearity  $\Delta E_{BL}$  [kcal/mol] of triplet  $\text{CH}_2$  (difference of energies between bent **2** and linear **1** from Table 1) and singlet  $\text{CH}_2$  ( $\Delta E$  of bent **4** and linear **3** from Table 2).

CCSD(T) Basis set	$\Delta E_{BL}$ ( <b>2</b> - <b>1</b> ) Triplet	$\Delta E_{BL}$ ( <b>4</b> - <b>3</b> ) Singlet
cc-pVDZ	6.8460	34.3662
cc-pVTZ	5.9017	31.8179
cc-pVQZ	5.7323	31.1860
cc-pV5Z	5.6660	30.8850
<b>CBS limit</b>	<b>5.6234</b>	<b>30.8422</b>
MCI CAS AE:	5.9 [49]	CMCI: 25.160 [48]
Experiment	$5.54 \pm 0.23$ [8]	$24.59 \pm 1.14$ [50]
Experiment	5.478 [9]	26.88 [51]

### Correlation Energies

The energy of correlation between electrons ( $\Delta E_{\text{corr}}$ ) is defined as  $\Delta E_{\text{corr}} = E_{\text{post-HF}} - E_{\text{HF}}$ , where  $E_{\text{post-HF}}$  is the total energy calculated by post-HF methods at maximum approaching the exact non-relativistic total energy of the system of interest and  $E_{\text{HF}}$  its the reference Hartree-Fock energy calculated under same conditions. In Table 8 we present the basis set dependence of our CCSD(T) values for correlation energies ( $\Delta E_{\text{corr}}$ ) of the methylenes **1** to **4**. In each case increases this energy with increase of basis set. This demonstrates the fact that increase of basis sets in the CCSD(T) methods leads to more effective treatment of electron correlation.

**Table 8.** Correlation energies obtained as the difference between CCSD(T) and Hartree-Fock total energies [Hartree] ( $\Delta E_{\text{correl}} = E_{\text{HF}} - E_{\text{cc-pVXZ}}$ ) from our cc-pVXZ (X= 2 – 5) calculations and extrapolations to the CBS limit.

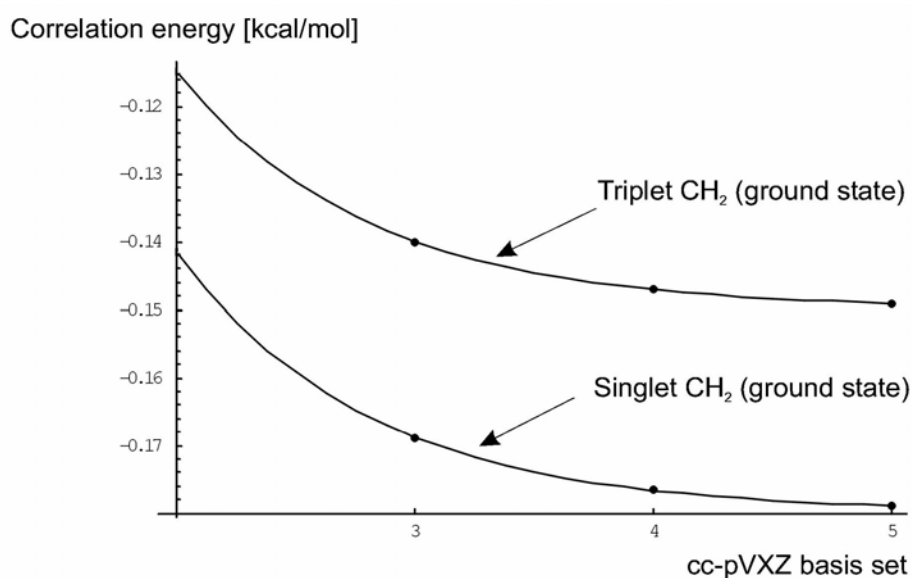
Molecule	Basis set	$\Delta E_{\text{correl}}$ [Hartree]
<sup>3</sup> B <sub>1</sub> CH <sub>2</sub> bent <b>1</b> triplet (ground state)	cc-pVDZ	-0.114976
	cc-pVTZ	-0.139995
	cc-pVQZ	-0.146980
	cc-pV5Z	-0.149101
	<b>CBS limit</b>	<b>-0.150026</b>
<sup>3</sup> Σ <sup>-</sup> CH <sub>2</sub> <b>2</b> triplet (linear)	cc-pVDZ	-0.116565
	cc-pVTZ	-0.142558
	cc-pVQZ	-0.149845
	cc-pV5Z	-0.152062
	<b>CBS limit</b>	<b>-0.153032</b>

Table 8. Cont.

Molecule	Basis set	$\Delta E_{\text{correl}}$ [Hartree]
$^1A_1$ CH <sub>2</sub> bent <b>3</b> singlet (ground state)	cc-pVDZ	-0.141485
	cc-pVTZ	-0.168839
	cc-pVQZ	-0.176555
	cc-pV5Z	-0.178935
	CBS limit	<b>-0.179997</b>
$^1\Delta_g$ CH <sub>2</sub> <b>4</b> Singlet (linear)	cc-pVDZ	-0.144840
	cc-pVTZ	-0.173029
	cc-pVQZ	-0.181233
	cc-pV5Z	-0.183755
	CBS limit	<b>-0.184875</b>

Again the exponential extrapolation procedure of eqn. 1 could be used to obtain CBS limits of the correlation energy. This behaviour is presented graphically in Fig. 2.

**Figure 2.** Exponential behaviour of correlation energies of the triplet  $^3B_1$  ground state of CH<sub>2</sub> (**1**) and the singlet  $^1A_1$  lowest state of CH<sub>2</sub> (**3**).



The correlation energy of the ground state singlet CH<sub>2</sub> (**3**) is substantially larger than that of the ground state triplet CH<sub>2</sub> (**1**) leading to a difference of the correlation energy between **1** and **3** of 18.81 kcal/mol. The same behaviour is observed for the linear conformations of singlet (**4**) and triplet (**2**) CH<sub>2</sub>. The difference of the correlation energy in the basis set limit is by 19.98 kcal/mol larger for **4** compared to **2**. The linear singlet CH<sub>2</sub> **4** shows the largest amount of correlation energy of the four considered species.

## Conclusions

The calculations of energies and structural parameters of methylene stationary points **1** to **4** attempt to complete existent coupled cluster CCSD(T) values of the literature by extrapolated Dunning values



in the basis set limit. Exponential extrapolations via the empirical eqn. 1 are possible for equilibrium distances, total energies, barriers to linearity, singlet-triplet separation energies and correlation energies but not for our valence angles.

Detailed comparison to the Dunning basis set dependence of other published post-HF calculations shows that the CCSD(T) method is in its Dunning basis set extrapolations a highly effective and reliable method for treatment of electron correlation of post-HF calculations. Only core-valence all electron correlations lead to lower total energies which proves the quality of the here used CCSD(T) calculations.

## References

1. Shavitt, I. Geometry and Singlet-Triplet Energy Gap in Methylene: A Critical Review of Experimental and Theoretical Determinations. *Tetrahedron* **1985**, *41*, 1531-1542.
2. Goddard III, W. A. Theoretical Chemistry Comes Alive: Full Partner with Experiment. *Science* **1985**, *227*, 917-923.
3. Schaefer III, H. F. Methylene: A Paradigm for Computational Quantum Chemistry. *Science* **1986**, *231*, 1100-1107.
4. Sherill, C. D.; Van Huis, T. J.; Yamaguchi, Y.; Schaefer III, H. F. Full Configuration Interaction Benchmarks for the  $\tilde{X}^3B_1$ ,  $\tilde{a}^1A_1$ ,  $\tilde{b}^1B_1$  and  $\tilde{c}^1A_1$  States of Methylene. *J. Mol. Struct. (Theochem)* **1997**, *400*, 130-156.
5. Foster, J. M.; Boys, S. F. Quantum Variational Calculations for a Range of CH<sub>2</sub> Configurations. *Rev. Mol. Phys.* **1960**, *32*, 305-307.
6. Herzberg, G.; Shoesmith, J. Spectrum and Structure of the Free Methylene Radical. *Nature* **1959**, *183*, 1801-1802.
7. Herzberg, G., Johns, J. W. C. On the Structure of CH<sub>2</sub> in its Triplet State. *J. Chem. Phys.* **1971**, *54*, 2276-2278.
8. Bunker, P. R.; Jensen, P. A Refined Potential Surface for the  $\tilde{X}^3B_1$  Electronic State of Methylene CH<sub>2</sub>. *J. Chem. Phys.* **1983**, *79*, 1224-1228.
9. Jensen, P.; Bunker, P. R. The Potential Surface and Stretching Frequencies of  $X^3B_1$  Methylene (CH<sub>2</sub>) Determined from Experiment Using the Morse Oscillator-Rigid Bender Internal Dynamic Hamiltonian. *J. Chem. Phys.* **1988**, *89*, 1327-1332.
10. Petek, H.; Nesbitt, D. J.; Darwin, D. C.; Ogilby, P. R.; Moore, C. B. Analysis of CH<sub>2</sub>  $\tilde{a}^1A_1$  (1,0,0) and (0,0,1) Coriolis-Coupled States,  $\tilde{a}^1A_1 - \tilde{X}^3B_1$  Spin-Orbit Coupling, and the Equilibrium Structure of CH<sub>2</sub>  $\tilde{a}^1A_1$  State. *J. Chem. Phys.* **1989**, *91*, 6566-6578.
11. Helgaker, T.; Joergensen, P.; Olsen, J. *Molecular Electronic Structure Theory*; Wiley: Chichester, New York, **2000**.
12. Purvis III, G. D.; Bartlett, R. J. A Full Coupled-Cluster Singles and Doubles Model: The Inclusion of Disconnected Triples. *J. Chem. Phys.* **1982**, *76*, 1910-1918.
13. Raghavachari, K.; Trucks, G. W., Pople J. A.; Head-Gordon, M. A Fifth Order Perturbation Comparison of Electron Correlation Theories. *Chem. Phys. Lett.* **1989**, *157*, 479-483.
14. Dunning, Jr., T. H. Gaussian Basis Functions for Use in Molecular Calculations I. Contraction of (9s,5p) Atomic Basis Sets for the First Row Atoms. *J. Chem. Phys.* **1970**, *53*, 2823-2833.

15. Dunning, Jr., T. H. Gaussian Basis Sets for Use in Correlated Molecular Calculations I. The Atoms Boron through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007-1023.
16. Almlöf, J.; Taylor, P. R. General Contraction of Gaussian Basis Sets. I. Atomic Natural Orbitals for First- and Second-Row Atoms. *J. Chem. Phys.* **1987**, *86*, 4070-4077.
17. Almlöf, J.; Taylor, P. R. Atomic Natural Orbital (ANO) Basis Sets for Quantum Chemical Calculations. *Adv. Quantum Chem.* **1992**, *22*, 301-373.
18. Helgaker, T.; Taylor, P. R. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific: Singapore, **1995**.
19. O'Neil, S. V.; Schaefer III, H. F.; Bender, C. F.  $C_{2v}$  Potential Energy Surfaces for Seven Low-Lying States of  $CH_2$ . *J. Chem. Phys.* **1971**, *55*, 162-169.
20. Alexander, S. A.; McDonald, C.; Matsen, F. A. Ab Initio Surfaces of Singlet and Triplet Methylene. *Int. J. Quantum Chem.* **1983**, *17*, 407-414.
21. Comeau, D. C.; Shavitt, I.; Jensen, P.; Bunker, P. R. Ab initio Determination of the Potential-Energy Surfaces and Rotation-Vibration Levels of Methylene in the Lowest Triplet and Singlet States and the Singlet-Triplet Splitting. *J. Chem. Phys.* **1989**, *90*, 6491-6500.
22. Yu, J.-S.; Chen, S.-Y.; Yu, C.-H. Analytical Fittings for the Global Potential Energy Surface of the Ground State of Methylene. *J. Chem. Phys.* **2003**, *118*, 582-594.
23. Bauschlicher, Jr., C. W.; Taylor, P. R. A Full CI Treatment of the  $^1A_1$ - $^3B_1$  Separation in Methylene. *J. Chem. Phys.* **1986**, *85*, 6510-6512.
24. Bauschlicher, Jr., C. W.; Taylor, P. R. Full CI Benchmark Calculations for Several States of the Same Symmetry. *J. Chem. Phys.* **1987**, *86*, 2844-2848.
25. Bauschlicher, Jr., C. W.; Langhoff, S. R.; Taylor, P. R.  $^1A_1$ - $^3B_1$  Separation in  $CH_2$  and  $SiH_2$ . *J. Chem. Phys.* **1987**, *87*, 387-391.
26. Bauschlicher, Jr., C. W.; Langhoff, S. R.; Taylor, P. R. Core-Core and Core-Valence Correlation. *J. Chem. Phys.* **1988**, *88*, 2540-2546.
27. Woon, D. E.; Dunning, T. H. Gaussian Basis Sets for Use in Correlated Molecular Calculations. V. Core-Valence Basis Sets for Boron through Neon. *J. Chem. Phys.* **1995**, *103*, 4572-4585.
28. Peterson, K. A.; Dunning, Jr., T. H. Benchmark Calculations with Correlated Molecular Wave Functions. Bond Energies and Equilibrium Geometries of the  $CH_n$  and  $C_2H_n$  ( $n = 1-4$ ) Series. *J. Chem. Phys.* **1997**, *106*, 4119-4140.
29. Sherrill, C. D.; Leininger, M. L.; Van Huis, T. J.; Schaefer III, H. F. Structures and Vibrational Frequencies in the Full Configuration Interaction Limit: Predictions of Four Electronic States of Methylene Using a Triple-Zeta Plus Double Polarization (TZ2P) Basis. *J. Chem. Phys.* **1998**, *108*, 1040-1049.
30. Császár, A. G.; Leininger, M. L.; Szalay, V. The Standard Enthalpy of Formation of  $CH_2$ . *J. Chem. Phys.* **2003**, *118*, 10631-10641.
31. Feller, D. Application of Systematic Sequences of Wave Functions of the Water Dimer. *J. Chem. Phys.* **1992**, *96*, 6104-6114.
32. Neugebauer, A.; Häfelfinger, G. Prediction of Experimentally Unknown  $r_e$ -Distances of Organic Molecules from Dunning Basis Set Extrapolations for ab initio Post-HF Calculations. *J. Phys. Org. Chem.* **2005**, in print.

33. Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley-VCH: Weinheim, New York, **1999**.
34. Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648-5652.
35. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, J. A.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, D. J.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98, Revision A.7*; Gaussian, Inc.: Pittsburgh, PA, **1998**.
36. Pauling, L.; Wilson, E. B. *Introduction to Quantum Mechanics with Applications to Chemistry*; McGraw-Hill: New York, **1935**.
37. Coulson, C. A. *Valence*; 2<sup>nd</sup> Ed.; Oxford University Press: Oxford, U.K., **1961**.
38. Langhoff, S. R.; Davidson, E. R. Configuration Interaction Calculations on the Nitrogen Molecule. *Internat. J. Quantum. Chem.* **1974**, *8*, 61-72.
39. Zittel, P. F.; Ellison, G. B.; O'Neil, S. V.; Herbst, E.; Lineberger, W. C.; Reinhardt, W. P. Laser Photoelectron Spectrometry of CH<sub>2</sub><sup>-</sup>. Singlet-Triplet Splitting and Electron Affinity of CH<sub>2</sub>. *J. Am. Chem. Soc.* **1976**, *98*, 3731-3732.
40. Hay, P. J.; Hunt, W. J.; Goddard III, W. A. Generalized Valence Bond Wave Functions for the Low Lying States of Methylene. *Chem. Phys. Lett.* **1972**, *13*, 30-35.
41. Bender, C. F.; Schaefer III, H. F.; Franceschetti, D. R.; Allen, L. C. Singlet-Triplet Energy Separation, Walsh-Mulliken Diagrams, and Singlet d-Polarization Effects in Methylene. *J. Am. Chem. Soc.* **1972**, *94*, 6888-6893.
42. Harding, L. B.; Goddard III, W. A. Methylene: ab initio Vibronic Analysis and Reinterpretation of the Spectroscopic and Negative Ion Photoelectron Experiments. *Chem. Phys. Lett.* **1978**, *55*, 217-220.
43. Leopold, D. G.; Murray, K. K.; Lineberger, W. C. Laser Photoelectron Spectroscopy of Vibrationally Relaxed CH<sub>2</sub><sup>-</sup>: A Reinvestigation of the Singlet-Triplet Splitting in Methylene. *J. Chem. Phys.* **1984**, *81*, 1048-1050.
44. McKellar, A. R. W.; Bunker, P. R.; Sears, T. J.; Evenson, K. M.; Saykally, R. J.; Langhoff, S. R. Far Infrared Laser Magnetic Resonance of Singlet Methylene: Singlet-Triplet Perturbations, Singlet-Triplet Transitions, and the Singlet-Triplet Splitting. *J. Chem. Phys.* **1983**, *79*, 5251-5264.
45. Sears, T. J.; Bunker, P. R. A Reinterpretation of the CH<sub>2</sub><sup>-</sup> Photoelectron Spectrum. *J. Chem. Phys.* **1983**, *79*, 5265-5271.
46. McLean, A. D.; Bunker, P. R.; Escribano, R. M.; Jensen, P. An ab initio Calculation of v<sub>1</sub> and v<sub>3</sub> for Triplet Methylene ( $\tilde{X}^3B_1$  CH<sub>2</sub>) and the Determination of the Vibrationless Singlet-Triplet Splitting T<sub>e</sub>( $\tilde{a}^1A_1$ ). *J. Chem. Phys.* **1987**, *87*, 2166-2169.

47. Gu, J.-P.; Hirsch, G.; Buenker, R. J.; Brumm, M.; Osmann, G.; Bunker, P. R.; Jensen, P. A. Theoretical Study of the Absorption Spectrum of Singlet CH<sub>2</sub>. *J. Molec. Struct.* **2000**, *517+518*, 247–264.
48. Green Jr., W. H.; Handy, N. C.; Knowles, P. J.; Carter, S. Theoretical Assignment of the Visible Spectrum of Singlet Methylene. *J. Chem. Phys.* **1991**, *94*, 118-132.
49. Harding, L. B.; Guadagnini, R.; Schatz, G. C. Theoretical Study of the Reactions H + CH → C + H<sub>2</sub> and C + H<sub>2</sub> → CH<sub>2</sub> Using an ab initio Global Ground-State Potential Surface for CH<sub>2</sub>. *J. Phys. Chem.* **1993**, *97*, 5472-5481.
50. Hartland, G. V.; Qin, D.; Dai, H.-L. Renner-Teller Effect on the Highly Excited Bending Levels of  $\tilde{a}^1A_1$  CH<sub>2</sub>. *J. Chem. Phys.* **1995**, *102*, 6641-6645.
51. Duxbury, G.; Alijah, A.; McDonald, B. D.; Jungen, C. Stretch-Bender Calculations of the Effects of Orbital Angular Momentum and Vibrational Resonances in the Spectrum of Singlet Methylene. *J. Chem. Phys.* **1998**, *108*, 2351-2360.
52. Yamaguchi, Y., Sherill, C. D.; Schaefer III, H. F. The  $\tilde{X}^3B_1$ ,  $\tilde{a}^1A_1$ ,  $\tilde{b}^1B_1$  and  $\tilde{c}^1A_1$  Electronic States of CH<sub>2</sub>. *J. Phys. Chem.* **1996**, *100*, 7911-7918.