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Accurate *ab initio* computation of thermochemical data for C_3H_x $(x = 0, \ldots, 4)$ species

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Dedicated to Professor Dr. Peter Botschwina on the occasion of his 60th birthday.

Abstract

We have computed the atomization energies of nineteen C_3H_x molecules and radicals using explicitly-correlated coupled-cluster theory including corrections for core–core and core–valence correlation, scalar and spin–orbit relativistic effects, and anharmonic vibrational zero-point energies. Equilibrium geometries were obtained at the coupled-cluster level [CCSD(T) model] in a correlation-consistent polarized core–valence quadruple-zeta basis set, using a spin-restricted Hartree–Fock reference wave function, and including all electrons in the correlation treatment. Applied to a set of selected CH_x and C_2H_x systems, our approach yields highly accurate atomization energies with a mean absolute deviation of 1.4 kJ/mol and a maximum deviation of 4.2 kJ/mol (for dicarbon) from the Active Thermochemical Tables (ATcT) values. The explicitly-correlated coupled-cluster approach provides energies near the basis-set limit of the CCSD(T) model, which is the coupled-cluster model with single and double excitations (CCSD) augmented with a perturbative correction for triple excitations (T). To obtain even more accurate atomization energies than those presented here, it would be required to include full triple excitations (CCSDT) and corrections for excitations beyond triples, as for instance done in the CCSDT(Q) model, which includes a perturbative correction for quadruple excitations (Q).
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1. Introduction

C_3H_x species with $x = 0, \ldots, 4$ play an important role in the formation and growth of polycyclic aromatic hydrocarbons (PAHs), in particular of small PAHs such as benzene and naphthalene during combustion or pyrolysis [1–8]. The self reaction of the propargyl radical (2-propynyl, CH_2CCH), for example, is thought to be the dominant reaction leading to the formation of benzene [4,7]. Reactions of phenyl radicals with propyne [9] or vinyl acetylene [10] may lead to naphthalene, and so on. Since many C_3H_3 and C_3H_x isomers are involved in the formation of PAHs and soot, the modeling of their formation under pyrolysis conditions requires the accurate knowledge of thermochemical data and rate constants of hundreds of species and elementary reactions [11,12].

Furthermore, C_3H_x species have been observed in interstellar space [13]. Examples are tricarbon (C_3), [14] linear [15] and cyclic C_3H, [16] propadienylidene and cyclopropenylidene [17,18].

Ab initio quantum chemical calculations can provide very accurate structural, spectroscopic and energetic data of small polyatomic molecules, radicals and carbenes of relevance to interstellar cloud chemistry and combustion processes. Particularly successful have been calculations

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employing the coupled-cluster method that includes single and double excitations (CCSD, cf. Refs. [19,20]) as well as a perturbative treatment of triple excitations [CCSD(T), cf. Refs. [21–25]]. Examples of such successes can be found in Refs. [26–30].

The present article is concerned with the highly accurate calculation of the equilibrium structures and ground-state energies of the C_3H_x species with $x = 0, \ldots, 4$. In the present work, the same set of molecules and radicals as studied by Vereecken and co-workers [31] at the level of density-functional theory will be investigated at the CCSD(T) level. Corrections for core–core and core–valence correlation effects, anharmonic zero-point vibrational energies and relativistic effects (both scalar and spin–orbit effects) will be taken into account in an attempt to compute the atomization energies of the species studied with chemical accuracy, that is, accurate to within 1 kcal/mol, respectively 4 kJ/mol. Here, accuracy refers to a 95% confidence limit. This means that atomization energies must be calculated with a mean absolute deviation of 1–2 kJ/mol from experimental data (*vide infra*). Such accuracy can only be achieved by performing the CCSD(T) calculations in very large and nearly complete one-electron basis sets, followed by basis-set extrapolation, [32–34] or by expanding the coupled-cluster wavefunction in a many-electron basis that contains terms that depend explicitly on the interelectronic distances in the system [35–37].

Very recently, Wheeler and co-workers published very accurate calculations of the enthalpies of formation of the following four key intermediates in soot formation: propargyl, 1-propynyl, cycloprop-1-enyl, and cycloprop-2-enyl [8]. These authors used the CCSD(T) method in conjunction with basis-set extrapolation techniques, that is, in the framework of the focal-point analysis [38,39] and also added corrections for core–core and core–valence correlation effects, anharmonic zero-point vibrational energies and relativistic effects. They even added diagonal Born–Oppenheimer corrections and correlation effects from triple excitations beyond the CCSD(T) level as obtained at the full CCSDT model, and from quadruple excitations as described at the CCSDT(Q) level [40].

The purpose of the present work is to provide highly accurate thermochemical data (i.e., atomization energies) for the above four key intermediates as well as for a number of other C_3H_x species from explicitly-correlated coupled-cluster calculations, that is, without resorting to basis-set extrapolation techniques, [32–34] and to obtain the equilibrium geometries at a CCSD(T) coupled-cluster level at the limits of what is technically feasible today (i.e., CCSD(T) calculations correlating all electrons in a correlation-consistent polarized core–valence quadruple-zeta basis).

Explicitly-correlated coupled electron-pair approximation and coupled-cluster methods were developed in the early 1990s for closed-shell atoms and molecules [41–45]. The general theory of the explicitly-correlated coupled-cluster theory is described in detail in Ref. [43] and a number of review articles exist [35–37]. In 2000, the theory was extended to single-reference open-shell cases with unrestricted Hartree–Fock (UHF) and restricted open-shell Hartree–Fock (ROHF) reference determinants [46,47].

Recent illustrative applications of explicitly-correlated coupled-cluster theory are reported in Refs. [48–54]. In all of these works, the explicitly-correlated coupled-cluster approach was used with two-electron basis functions that are linear in the interelectronic distance. In conjunction with very large one-electron basis sets, such a linear r_{12} approach yields benchmark results near the limit of a complete basis set, as demonstrated for example in Refs. [53,54]. Since a few years, however, several research groups have started to develop explicitly-correlated coupled-cluster approaches with Slater-type geminals (STGs), first proposed by Tenno in 2004 [55–58]. The main advantage of using STGs in place of the linear r_{12} terms is that in the STG approach much smaller one-electron basis sets may be used than in the linear r_{12} approach. Because only linear r_{12} coupled-cluster approaches have been implemented for open-shell systems, only these approaches could be used in the present work, using very large basis sets. We expect that the results presented in the present article may serve as benchmark data for future calculations using STGs and smaller basis sets.

The present paper is organized as follows: The computational details of all of our calculations are described in Section 2. The results for the C_3H_x species are presented in Section 3. This section also contains computed thermochemical data for the CH_x and C_2H_x systems in comparison with the Active Thermochemical Tables (*vide infra*) to highlight the accuracy of the *ab initio* calculations (Section 3.1). Conclusions are given in Section 4.

2. Computational details

2.1. Basis sets

The standard CCSD(T) coupled-cluster calculations were performed in correlation-consistent polarized core–valence basis sets of triple-(cc-pCVTZ′) and quadruple-zeta (cc-pCVQZ′) quality [59,60]. We have attached a prime to these sets to indicate that cc-pCVTZ′ refers to the basis cc-pCVTZ for C, but only cc-pVDZ for H. Similarly, the cc-pCVQZ′ refers to the basis cc-pCVQZ for C, but only cc-pVTZ for H.

The effect of using the "primed" basis sets in place of the full basis sets, that is, the effect of using basis sets with a smaller cardinal number for H than for C, has been investigated in detail for the molecules CH ($^2\Pi$ state), CH_2 ($^3B_1$ state) and CH_4 ($^1A_1$). Concerning the equilibrium geometries of these molecules, we find that in the cc-pCVQZ′ basis, the C–H bond lengths are 0.1 pm longer than in the full cc-pCVQZ basis (in CH_2, the H–C–H angle is reduced by 0.06° in the full cc-pCVQZ basis). Moreover, we can compare our cc-pCVQZ′ geometry of singlet propadienylidene with the equilibrium geometry obtained by Gauss and Stanton in the full cc-pCVQZ basis [61]. The only significant difference between the two geometries is

the C–H distance, which is 0.1 pm longer in the cc-pCVQZ′ basis (see also Section 3.2.6).

The effect of the cc-pCVQZ′ basis on the correction for core- and core–valence (CV) correlation effects (*vide infra*) is almost negligible. For CH, the "primed" basis yields a CV correction to the atomization energy that is 0.03 kJ/mol smaller than in the full cc-pCVQZ basis. For triplet methylene and methane, the corresponding reductions are 0.06 and 0.13 kJ/mol, respectively. Hence, we expect that the effect on the CV correction will be of the order of 0.1 kJ/mol for most of the molecules studied (ca. 0.03 kJ/mol per H atom).

The impact of the "primed" basis on the zero-point vibrational energy is more important than on the CV correction. This is not surprising, because only a small cc-pVDZ basis is used for H in the cc-pCVTZ′ basis. In the "primed" basis, the zero-point vibrational energies of CH, CH_2 and CH_4 are 0.28, 0.55 and 1.6 kJ/mol, respectively, smaller than in the full basis. Hence, the effect may be of the order of 1–2 kJ/mol for molecules with up to four C–H bonds.

The explicitly-correlated CCSD(T)-R12 calculations were carried out in the basis 19s14p8d6f4g3h for C and 9s6p4d3f for H, taken from Ref. [62]. For a molecule such as C_3H_4, this basis comprises 908 spherical Gaussian orbitals. For CH, triplet CH_2 and CH_4, we computed their CCSD(T)-R12 energies at the cc-pCVQZ′ and cc-pCVQZ equilibrium geometries. The energy differences were below 0.02 kJ/mol and can be neglected.

2.2. Methods and programs

The backbone of our computational procedure is the calculation of the CCSD(T)(FC)-R12 energy in the large C = 19s14p8d6f4g3h/H = 9s6p4d3f Gaussian basis of Section 2.1 at CCSD(T)(Full)/cc-pCVQZ′ optimized geometries. In these coupled-cluster calculations, that is, in the CCSD(T)(Full)/cc-pCVQZ′ geometry optimizations as well as in the CCSD(T)(FC)-R12 single-point energy calculations, we have used restricted (open-shell) Hartree–Fock reference wave functions (RHF or ROHF) and semicanonical orbitals for the (T) triples correction [25].

Several corrections were added to these raw data. These corrections are: (i) Energy corrections due to including core orbitals in the correlation treatment (denoted CV); (ii) Corrections due to zero-point vibrational energy (E_{ZPVE}), which consists of harmonic (Harm.) and anharmonic (Anharm.) contributions; (iii) First-order spin–orbit contributions (E_{SO}), which arise from the atomic states involved; (iv) First-order scalar relativistic effects (E_{SR}) due to the one-electron Darwin and mass–velocity (Ms.–Vel.) operators.

Due to hardware restrictions, although we used the improved algorithm for triple-excitation contributions of Noga and Valiron, [63] the contribution from the valence-shell (T) connected triples could not always be computed at the CCSD(T)(FC)-R12 level in the large C = 19s14p8d6f4g3h/H = 9s6p4d3f basis. In cases where this calculation was impossible, the triples correction was computed at the conventional CCSD(T)(FC) level in the cc-pCVQZ′ basis. A comparison of the (T) values from both types of calculations (where available) showed that the CCSD(T)(FC)-R12 triples correction adds about 0.36 kJ/mol per C atom to the atomization energy more than the conventional CCSD(T)(FC) correction. Hence, we have added an empirical 0.36 kJ/mol per C atom to the atomization energy on the occasions where the triples corrections were computed at the CCSD(T)(FC)/cc-pCVQZ′ level.

The CV correction was obtained from the difference between the CCSD(T)(Full)/cc-pCVQZ′ and CCSD(T)-(FC)/cc-pCVQZ′ energies at the CCSD(T)(Full)/cc-pCVQZ′ optimized geometries. Here, (FC) indicates that the core orbitals (1s on C) were kept frozen, whereas (Full) indicates that all orbitals were included in the correlation treatment.

The harmonic zero-point vibrational energy was computed at the CCSD(T)(Full)/cc-pCVTZ′ level using RHF reference wave functions for closed-shell and UHF reference wave functions for open-shell molecules [64,65].

The anharmonic correction to the zero-point energies were calculated at the DFT (density-functional theory) level. Concerning the force field, we followed the approach proposed by Schneider and Thiel, [66] in which a full cubic and a semidiagonal quartic force field are obtained by central numerical differentiation (in rectilinear normal coordinates about the equilibrium geometry) of analytical second derivatives. The latter were obtained by means of locally modified versions of Gaussian98 [67]. Modified routines from Cadpac [68] were used as the driver for the numerical differentiation routine [69,70]. These calculations have been performed with the B97-1 functional [71] and the TZ2P basis sets [72]. These are Dunning [73] contractions of Huzinaga [74] primitive sets. For C, it is a 11s6p to 5s4p contraction with two sets of polarization functions with exponents 1.2 and 0.4. For H the contraction is 5s to 3s and the two sets of polarization functions have exponents 1.5 and 0.5. All of the force fields were analyzed by means of the Spectro [75] and Polyad [76] rovibrational perturbation theory programs. In this way, the G_0 term has been included into the calculation of the anharmonic correction to the ZPVE.

For a test set of 15 closed-shell molecules plus CH_2 and NH_2, we obtained a root-mean-square error of 0.2 kJ/mol for the anharmonic correction employing this scheme [69]. In some cases, the anharmonicity constants of the lowest torsion modes were physically unrealistic when determined by second-order perturbation theory. We therefore decoupled these modes by zeroing all off-diagonal anharmonicity constants involving them. For six molecules (CH, CH_3, C_2, C_3, triplet cyclopropenylidene, and singlet propadienylidene) the anharmonic correction to the zero-point vibrational energy was computed from third and fourth derivatives of the UHF–CCSD(T)(Full)/cc-pCVTZ′ energy by numerical differentiation of analytically calculated second derivatives, [64,65] as implemented in the Mainz–Austin–Budapest version of the program system Aces II [77].

The spin–orbit contributions (E_{SO}) were obtained from experimental atomic levels while the Darwin and mass–velocity energy corrections were computed analytically as first-order molecular property at the CCSD(T)(Full)/cc-pCVQZ′ level using the ACES II program.

All coupled-cluster calculations except for the CCSD(T)-R12 calculations were performed with the Mainz–Austin–Budapest version of the ACES II package of programs [77]. See also Ref. [78]. The CCSD(T)-R12 calculations were done with the DIRCCR12-OS program [79].

Finally, we note that not all equilibrium geometries could be determined at the CCSD(T)(Full)/cc-pCVQZ′ level using an ROHF reference determinant, partly for technical reasons and partly due to convergence problems. In particular, we did not succeed for the ^{3}A state of cyclopropenylidene (c-C_3H_2), the ^{3}B state of prop-2-ynylidene (HCCCH), and the ^{2}A″ states of 1- and 2-propene-1-yl-3-ylidene. For these four systems, we used the UHF–CCSD(T)/cc-pCVTZ′ equilibrium geometries. Furthermore, with the DIRCCR12-OS program, [79] we could not converge the ^{2}A″ ROHF wave function in the large C = 19s14p8d6f4g3h/H = 9s6p4d3f Gaussian basis of Section 2.1 for 1-propene-1-yl-3-ylidene. We used an UHF reference instead for this system.

2.3. Active Thermochemical Tables

Active Thermochemical Tables (ATcT) are a new paradigm of how to obtain accurate, reliable, and internally consistent thermochemical values by using all available knowledge [80–83] and overcome the limitations that are deeply engrained in the traditional approach to thermochemistry, such as that used in all traditional thermochemical compilations. As opposed to the traditional sequential approach, ATcT derives its results from a Thermochemical Network (TN). The thermochemical values used in the present work for the purpose of benchmarking the current method have been obtained from the latest version of the Core (Argonne) Thermochemical Network, C(A)TN, that is currently under development [84] and describes ca. 800 species interconnected by ca. 8000 experimental and theoretical determinations. For the species of interest here, the current version of C(A)TN includes all available experimental results and also considers a selection of prior highly accurate theoretical results, such as those by Karton et al. [34] (with weights proportional to the expected uncertainties), but does not include the present computational results. Full details of how these ATcT values were developed and what data they are based on will be published separately [85].

3. Results and discussion

3.1. CH_x and C_2H_x species

Accurate atomization energies, that is, the sum of all of the bond dissociation enthalpies at zero kelvin, $\sum D_0$ (0 K), are available for the small CH_x and C_2H_x species from the Active Thermochemical Tables (ATcT, cf. Section 2.3). The atomization energies are known with an accuracy of about ±0.3 kJ/mol or better. Only for the dicarbon molecule and the vinyl radical, the ATcT uncertainty is slightly larger (±0.6 and ±0.9 kJ/mol, respectively). The ATcT values are presented in Table 1, together with other experimental and computational data from the literature [86–94]. The ATcT uncertainties correspond to 95% confidence limits, as expected in thermochemistry (approximately equal to two standard deviations). Please note that, in general, before directly comparing the 95% confidence limits, which are the generally accepted measure of uncertainty in thermochemistry, with the mean absolute deviation (which is the prevailing measure of fidelity in electronic-structure theory), one of the two needs to be rescaled: either the 95% confidence limits need to be divided by a factor between two and three (2.5 if the distribution of errors is normal) or the mean absolute deviation needs to be multiplied by the same factor.

For these small molecules and radicals, the CCSD(T) level of theory as applied in the present work – including core-correlation, relativistic and anharmonic vibrational corrections – provides atomization energies (column "Calc." in Table 1) with a mean absolute deviation of 1.4 kJ/mol from the ATcT values (1 kcal/mol 95% confidence limit or 1–2 kJ/mol mean absolute deviation may be regarded as chemical accuracy). The CCSD(T) calculations of the C_2 molecule and the C_2H radical exhibit the largest errors (−4.2 and −3.8 kJ/mol, respectively). We have included the small CH_x and C_2H_x species in the present study to test the accuracy of the applied computational approach. For example, ZPVEs of diatomic molecules are accurately known from experiment. Concerning our systems, the experimental ZPVEs (including the often forgotten Dunham [95,96] Y_{00} term and spin–orbit coupling in form of a correction for the lowest *existing* rovibrational level) of CH and C_2 amount to 1416.2 cm^{-1} = 16.942 kJ/mol and 924.0 cm^{-1} = 11.053 kJ/mol, respectively [97]. They agree with the calculated values (16.56 kJ/mol and 11.06 kJ/mol) to within 0.4 kJ/mol.

The electronic structures of (some of) the C_3H_x species are significantly more complex than those of the small C1 and C2 systems. Therefore, we may not expect that the computational data presented in Section 3.2 are accurate to within a mean absolute deviation of 1.4 kJ/mol. Nevertheless, we believe that an accuracy very close to chemical accuracy is a realistic assumption.

In the following section, we shall discuss all of the nineteen C_3H_x species in some detail. All of these species have already been investigated on several occasions by other researchers and we shall compare our results with the corresponding data from the literature. These comparisons also reassure us that we have optimized the appropriate equilibrium structures (point-group symmetries) and electronic states (cf. Fig. 1).

Table 1
CH_x and C_2H_x ($x = 0, \ldots, 4$) isomers: Frozen-core (FC) and core–valence (CV) contributions to the equilibrium atomization energy D_e (0 K), harmonic (Harm.) and anharmonic (Anharm.) zero-point vibrational energy contributions E_{ZPVE}, spin–orbit energy contributions E_{SO}, first-order Darwin (Darwin) and mass–velocity (Ms.–Vel.) scalar relativistic energy contributions E_{SR}, and calculated (Calc.) and experimental or previous theoretical (Exptl./Theor.) atomization energy $\sum D_0$ (0 K)

Species	State	D_e (0 K)		E_{ZPVE}		E_{SO}	E_{SR}		$\sum D_0$ (0 K)		
		FC	CV	Harm.	Anharm.		Darwin	Ms.–Vel.	Calc.	ATcT[a]	Exptl./Theor.
Methylidyne, CH	$^2\Pi$	350.93	0.61	−16.74	0.18[b]	−0.35	0.38	−0.55	334.45	334.65 ± 0.23	$334.74^{+0.13}_{-0.34}$[c]
Methylene, CH_2	$^3B_1$	794.15	3.15	−45.05	0.57	−0.35	1.68	−2.30	751.85	752.68 ± 0.26	$753.03^{+0.43}_{-0.62}$[d]
	$^1A_1$	755.72	1.56	−43.16	0.46	−0.35	0.88	−1.24	713.86	715.02 ± 0.26	$715.38^{+0.43}_{-0.62}$[d]
											713 ± 2[e]
Methyl, CH_3	$^2A_2''$	1 282.98	4.16	−77.32	0.90[b]	−0.35	1.89	−2.61	1 209.64	1 209.66 ± 0.14	1210.3 ± 0.9[f]
Methane, CH_4	$^1A_1$	1 753.10	4.88	−116.25	1.41	−0.35	2.08	−2.89	1 641.97	1 642.24 ± 0.12	1642.2 ± 0.6[f]
Dicarbon, C_2	$^1\Sigma_g^+$	606.96	3.96	−11.10	0.04[b]	−0.71	2.17	−2.91	598.42	602.60 ± 0.57	593 ± 4[f]
											601.2 ± 1.3[g]
											603.0 ± 0.7[h]
Ethynyl, C_2H	$^2\Sigma^+$	1 102.25	8.23	−38.15	0.75	−0.71	3.45	−4.61	1 071.20	1 074.99 ± 0.29	1075.1 ± 1.5[i]
Ethyne, C_2H_2	$^1\Sigma_g^+$	1 684.92	9.62	−69.17	0.77	−0.71	3.46	−4.63	1 624.27	1 626.10 ± 0.29	1619 ± 1[f]
											1627 ± 1[j]
Vinyl, C_2H_3	$^2A'$	1 855.21[k]	8.56	−95.49	1.24	−0.71	3.57	−4.86	1 767.53	1 768.24 ± 0.88	
Ethene, C_2H_4	^1A_g	2 349.01	9.24	−132.58	1.54	−0.71	3.78	−5.17	2 225.11	2 225.96 ± 0.26	2225.5 ± 0.7[f]

All values in kJ/mol.
[a] ATcT, Ref. [84].
[b] UHF–CCSD(T)(Full)/cc-pCVTZ′ value.
[c] Ref. [86].
[d] Ref. [87].
[e] See Ref. [88].
[f] Ref. [89].
[g] Ref. [90].
[h] Ref. [91].
[i] Ref. [92].
[j] Ref. [93].
[k] Valence-shell triples correction (T) computed in the cc-pCVQZ′ basis.

3.2. C_3H_x species

In the following subsections, we discuss each of the nineteen C_3H_x species in some detail. Their equilibrium geometries are depicted in Figs. 2 and 3.

3.2.1. Tricarbon, C_3

Tricarbon was investigated in great detail and accuracy at the CCSD(T) level by Mladenović et al. in 1994 [98]. These authors obtained an equilibrium C–C distance of 129.45 pm for the $^1\Sigma_g^+$ state in $D_{\infty h}$ symmetry. This is in full agreement with the CCSD(T)(Full)/cc-pCVQZ′ value of $r_e =$ 129.46 pm obtained in the present work, which is however slightly larger than the B3LYP/6-311 G(d,p) value of 129.1 pm [99,100]. Botschwina has argued that CCSD(T) calculations tend to overestimate the bond length of multiple CC bonds slightly (e.g., by 0.1 pm) and therefore has reported a recommended value for the CC bond length of C_3 of 129.36 ± 0.04 pm [101]. Our best estimate of the atomization energy amounts to 1316 kJ/mol, which is in agreement with the NIST–JANAF value of 1323 ± 17 kJ/mol to within the experimental uncertainty. It is furthermore noteworthy that we have been able to compute the anharmonic correction to the ZPVE (0.13 kJ/mol) at the UHF–CCSD(T)(Full)/cc-pCVTZ′ level and that the basis-set incompleteness correction to the atomization energy amounts to 14.5 kJ/mol. The latter correction is defined as the difference between the frozen-core CCSD(T)-R12 and CCSD(T)(FC)/cc-pCVQZ′ results, that is, it corrects for the basis-set incompleteness error of the cc-pCVQZ′ basis.

3.2.2. Cyclopropynylidyne, c-C_3H

We have computed the atomization energy of the cyclopropynylidyne radical in its $^2B_2$ ground state in C_{2v} symmetry, [102] with the molecule in the *yz* plane (concerning the symmetry conventions, see Ref. [103]). We have optimized the geometry in C_{2v} symmetry at the CCSD(T)(Full)/cc-pCVQZ′ level but use the accurate harmonic ZPVE of Stanton [104] obtained at the EOMIP–CCSD level to circumvent the problems related to the strong pseudo Jahn–Teller effects in the *c*-C_3H radical (note that the *anharmonic* contribution was obtained from DFT calculations). The CCSD(T)(Full)/cc-pCVQZ′ equilibrium distances (r_e(C—*H*) = 107.9 pm, r_e(C—CH) = 137.3 pm, and r_e(C—C) = 137.1 pm) compare to within 0.6 pm with the experimental r_s values of Yamamoto and Saito (107.6, 137.4, and 137.7 pm, respectively) [102].

We find the cyclopropynylidyne radical 8.4 kJ/mol below the linear isomer (*vide infra*). This is in line with the coupled-cluster results of other researchers, [105,106] who report the cyclic isomer 6.7–7.1 kJ/mol below the linear form.

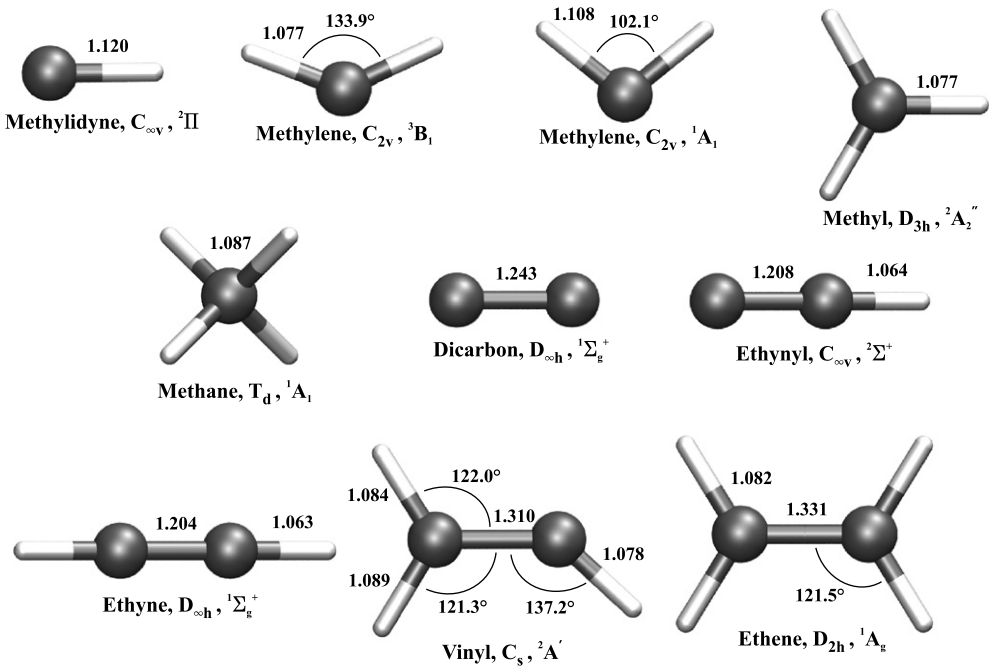

Fig. 1. ROHF–CCSD(T)(Full)/cc-pCVQZ′ optimized geometries of the CH_x and C_2H_x ($x = 0, \ldots, 4$) species of Table 1. All bond lengths in Å.

3.2.3. Propynylidyne, l-C_3H

Three isomers of C_3H are discussed in the literature; a cyclic *c*-C_3H (C_{2v} symmetry, *vide supra*), a linear *l*-C_3H ($C_{\infty v}$), and a bent *b*-C_3H (*trans*) form with C_s symmetry (cf. Ref. [106]). The two linear structures *l*-C_3H and *b*-C_3H are virtually isoenergetic with the *l*-C_3H radical ca. 0.8 kJ/mol below *b*-C_3H at the CCSD(T)/cc-pVQZ level [106]. Hence, we have restricted our CCSD(T)(Full)/cc-pCVQZ′ geometry optimization to the linear *l*-C_3H isomer (for technical reasons, the calculation was performed in C_{2v} symmetry). It is difficult to compute the vibrational frequencies and the ZPVE for the linear *l*-C_3H radical in its $^2\Pi$ state because no stable wave function can be determined with the right symmetry restrictions. Therefore, we follow the approach chosen by Ochsenfeld et al. [106] and adopt their CCSD(T)/TZP value for the *b*-C_3H isomer (43.98 kJ/mol). The anharmonic correction is crudely estimated to be of the same order of magnitude (0.4 kJ/mol) as for *c*-C_3H, which is sufficiently accurate in view of our target accuracy of ca. 4 kJ/mol and the remaining errors in the calculations. Our final atomization energy amounts to 1629 kJ/mol and contains an basis-set incompleteness correction of 18.8 kJ/mol.

3.2.4. Singlet cyclopropenylidene, c-C_3H_2

We have optimized the $^1A_1$ ground state of *c*-C_3H_2 in C_{2v} symmetry at the CCSD(T)(Full)/cc-pCVQZ′ level. The internuclear distances agree to within 0.7 pm with the coupled-cluster results of Sherill et al. [107] and to within 0.5 pm with those of Seburg et al. [108]. Furthermore, we obtain virtually the same harmonic ZPVE (84.3 kJ/mol) as in Ref. [108] (85.1 kJ/mol). Calculations of the $^1A_1$ state of cyclopropenylidene appear to be straightforward, and our final atomization energy of 2068 kJ/mol may be regarded as a reliable value. The correction for basis-set incompleteness contributes 25.4 kJ/mol to this atomization energy. Concerning the reaction

$$C_2H_3(^2A') + C(^3P) \rightarrow c\text{-}C_3H_2(^1A_1) + H(^2S). \quad (1)$$

Nguyen et al. report an exothermic energy of reaction (at 0 K) of −69.5 kcal/mol (−291 kJ/mol) at the CCSD(T)/6-311+G(3df,2p) level. We obtain −300 kJ/mol for this reaction energy (cf. Tables 1 and 2). The difference of 9 kJ/mol between these results can largely be traced back to the basis-set incompleteness and CV corrections (−5.5 and −3.4 kJ/mol) that are taken into account in the present work.

Clauberg et al. have reported an experimentally derived heat of formation of $\Delta_f H^0(298.15\ \mathrm{K}) = 114 \pm 4$ kcal/mol [109]. This value corresponds to a heat of reaction for the complete dissociation of $\Delta_r H^0(298.15\ \mathrm{K}) = 2109 \pm 17$ kJ/mol. Correcting for the difference $\Delta_r H^0(298.15\ \mathrm{K}) - \Delta_r H^0(0\ \mathrm{K}) = 21.6$ kJ/mol, which is estimated from the UHF–CCSD(T)/cc-pCVTZ′ harmonic vibrational frequencies and the experimental electronic energy levels of the C atom, the value of Clauberg et al. [109] yields an experimentally derived estimate of the atomization energy of singlet cyclopropenylidene of 2087 ± 17 kJ/mol. Our computed value is almost within the experimental uncertainty. Furthermore, Chyall and Squires have reported an experimentally derived $\Delta_f H^0(298.15\ \mathrm{K})$ of 119.5 ± 2.2 kcal/mol [110]. This value leads to an experimentally derived estimate of the atomization energy of 2064 ± 10 kJ/mol, in agreement with our CCSD(T)-R12 value of 2068 kJ/mol.

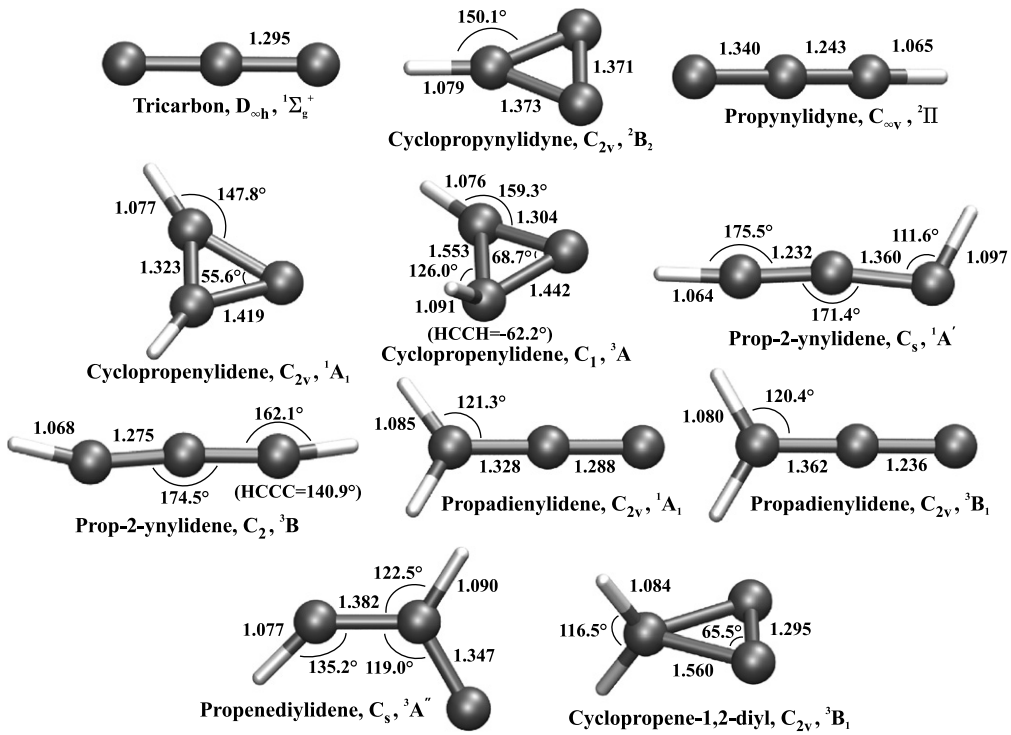

Fig. 2. ROHF–CCSD(T)(Full)/cc-pCVQZ′ optimized geometries of the C_3H_x ($x = 0, \ldots, 2$) species of Table 2. All bond lengths in Å. The ^{3}A state of cyclopropenylidene and the ^{3}B state of prop-2-ynylidene were optimized at the UHF–CCSD(T)(Full)/cc-pCVTZ′ level.

3.2.5. Triplet cyclopropenylidene, c-C_3H_2

Triplet cyclopropenylidene displays C_1 symmetry and a ^{3}A state [105,106]. Coupled-cluster calculations on this system are unproblematic and we were able to compute the anharmonic correction to the ZPVE at the UHF–CCSD(T)(Full)/cc-pCVTZ′ level. In our calculations, the triplet state of cyclopropenylidene lies 222 kJ/mol above the singlet ground state, and the energy of reaction (at 0 K) of the reaction

$$C_2H_3(^2A') + C(^3P) \rightarrow c\text{-}C_3H_2(^3A) + H(^2S) \quad (2)$$

hence amounts to −79 kJ/mol. Nguyen et al. [105] have reported −71 kJ/mol for this reaction and the difference between their value and ours can again largely be explained by the basis-set incompleteness and CV corrections, which contribute −3.7 and −2.9 kJ/mol, respectively, to the reaction energy of (2).

3.2.6. Singlet propadienylidene, CH_2CC

Propadienylidene has a $^1A_1$ ground state in C_{2v} symmetry [61,111]. Our CCSD(T)(Full)/cc-pCVQZ′ geometry optimization of this state is identical with the optimization carried out by Gauss and Stanton in 1999, [61] except that we have used the slightly smaller cc-pCVQZ′ basis instead of the full cc-pCVQZ basis, and except that nine years after their work it is technically feasible to compute the gradient analytically. Our analytical results are virtually in full agreement with the numerical results of Ref. [61] (only the C–H distance is 0.1 pm longer in our optimization). We have computed the harmonic and anharmonic ZPVE at the CCSD(T)(Full)/cc-pCVTZ′ level, and our final atomization energy (2009 kJ/mol) is probably very reliable. This translates into a reaction energy of −241 kJ/mol for the reaction

$$C_2H_3(^2A') + C(^3P) \rightarrow CH_2CC(^1A_1) + H(^2S). \quad (3)$$

The corresponding frozen-core value in a 6-311+G(3df,2p) basis is −234 kJ/mol, [105] which seems reasonable in view of the basis-set incompleteness and CV corrections (−2.6 and −2.5 kJ/mol).

3.2.7. Triplet propadienylidene, CH_2CC

In agreement with the works of Ochsenfeld et al. [106] and Rubio et al., [112] we find a $^3B_1$ state in C_{2v} symmetry for the lowest triplet state of propadienylidene (with the molecule in the *yz* plane). At the CCSD(T)/TZP level, Ochsenfeld et al. [106] find C–C equilibrium distances of 123.8 and 136.9 pm and a C–H distance of 108.1 pm. Their H–C–H angle amounts to 119.0°. At the CCSD(T)/cc-pCVQZ′ level applied in the present work, the corresponding structural data are 123.6 pm, 136.2 pm, 108.0 pm and 119.2°, respectively. The adiabatic singlet–triplet splitting of the propadienylidene diradical has been reported to 29.7 kcal/mol (124 kJ/mol) by Robinson et al., obtained from the photoelectron spectrum of the propadienylidene anion [113]. The difference between the atomization energies of the singlet and triplet species in Table 2 amounts to 124.2 kJ/mol (29.7 kcal/mol), which is in full agreement with the experimentally derived value.

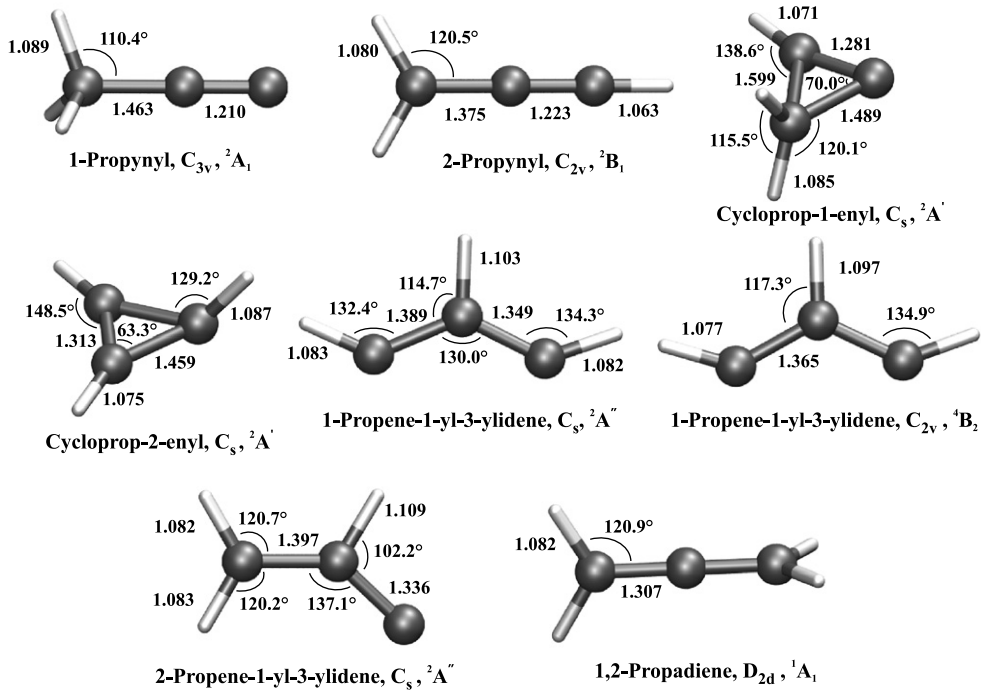

Fig. 3. ROHF–CCSD(T)(Full)/cc-pCVQZ′ optimized geometries of the C_3H_x ($x = 3, 4$) species of Table 3. All bond lengths in Å. The $^2A''$ states of 1-propene-1-yl-3-ylidene and 2-propene-1-yl-3-ylidene were optimized at the UHF–CCSD(T)(Full)/cc-pCVTZ′ level.

Table 2
C_3H_x ($x = 0, \ldots, 2$) isomers: frozen-core (FC) and core–valence (CV) contributions to the equilibrium atomization energy D_e (0 K), harmonic (Harm.) and anharmonic (Anharm.) zero-point vibrational energy contributions E_{ZPVE}, spin–orbit energy contributions E_{SO}, first-order Darwin (Darwin) and mass–velocity (Ms.–Vel.) scalar relativistic energy contributions E_{SR}, and calculated (Calc.) and experimental or previous theoretical (Exptl./Theor.) atomization energy $\sum D_0$ (0 K)

Species	State	D_e (0 K)		E_{ZPVE}		E_{SO}	E_{SR}		$\sum D_0$ (0 K)	
		FC	CV	Harm.	Anharm.		Darwin	Ms.–Vel.	Calc.	Exptl./Theor.
Tricarbon, C_3	$^1\Sigma_g^+$	1 330.93	7.86	−20.78	0.13[a]	−1.06	2.48	−3.29	1 316.27	1 323 ± 17[b]
Cyclopropynylidyne, c-C_3H	$^2B_2$	1 678.46[d]	10.88	−49.94[c]	0.38	−1.06	4.39	−5.93	1 637.17	
Propynylidyne, l-C_3H	$^2\Pi$	1 663.95[d]	10.75	−43.98[e]	0.40[f]	−1.06	3.92	−5.25	1 628.73	
Cyclopropenylidene, c-C_3H_2	$^1A_1$	2 142.16	11.93	−84.28	0.82	−1.06	4.72	−6.39	2 067.90	2064 ± 10[g]
	^3A[h]	1 915.59[d]	11.43	−78.94	1.18[a]	−1.06	5.05	−6.86	1 846.38	
Propadienylidene, CH_2CC	$^1A_1$	2 079.53	11.01	−80.18	0.83[a]	−1.06	4.11	−5.55	2 008.70	
	$^3B_1$	1 952.98[d]	12.72	−78.89	0.73	−1.06	5.53	−7.47	1 884.54	
Prop-2-ynylidene, HCCCH	$^1A'$	2 029.99	11.93	−72.64	0.78	−1.06	4.57	−6.16	1 967.41	
	^3B[h]	2 077.03[d]	13.60	−67.09	0.60	−1.06	5.41	−7.28	2 021.22	
Propenediylidene,[i] HCCHC	$^3A''$	1 831.01[d]	9.99	−71.87	0.16	−1.06	4.13	−5.60	1 767.44	
Cyclopropene-1,2-diyl, c-CH_2CC	$^3B_1$	1 846.61[d]	10.22	−82.94	0.80[f]	−1.06	4.61	−6.29	1 771.95	

All values in kJ/mol.
[a] UHF–CCSD(T)(Full)/cc-pCVTZ′ value.
[b] Ref. [89].
[c] Ref. [104].
[d] Valence-shell triples correction (T) computed in the cc-pCVQZ′ basis.
[e] Ref. [106].
[f] Estimated.
[g] Ref. [110]; see also the text.
[h] UHF–CCSD(T)/cc-pCVTZ′ optimized geometry.
[i] Trans isomer.

3.2.8. Singlet prop-2-ynylidene, HCCCH

Although the triplet is the ground state of prop-2-ynylidene (propargylene), the singlet has been studied in great detail in the literature because of the competition between two possible structures that lie very close in energy [114]. Furthermore, the singlet state can of course occur as initial product in (photo)chemical reactions. The two possible structures display C_{2v} and C_s symmetry and can be characterized as a 1,3-diradical and a classical carbene, respectively. In the latter, the two C–C bonds differ by ca.

13 pm. In 1999, Stanton and Byun found that at the CCSD(T) level in a 5s4p3d2f/4s3p2d atomic natural orbital basis set for C/H, the C_s structure lies 437 cm^{-1} (ca. 5 kJ/mol) below the C_{2v} structure. At the CCSDT level with full triples (but in a small 6-31G* basis) this difference is reduced to only 25 cm^{-1}. Similar results are obtained by Nguyen et al. [105] from CCSD(T)/6-311+G(3df,2p) calculations that predict the C_s structure 1.7 kJ/mol below the C_{2v} structure [105]. We note, however, that B3LYP/6-311G(d,p) calculations yield the opposite result with the 1,3-diradical C_{2v} structure 2.5 kJ/mol below the C_s carbene. Moreover, Rubio et al. [112] report that CASSCF geometry optimizations locate the C_s structure below the C_{2v} structure but that CASPT2 single-point calculations (performed at the CASSCF geometries) locate the C_{2v} structure 0.9 kJ/mol below the C_s structure. In any case, the C_{2v} and C_s structures are almost degenerate and for the present CCSD(T)-R12 calculations, we have decided to carry out calculations for the C_s structure, which is favored by CCSD(T) theory [114].

For the reaction

$$C_2H_3(^2A') + C(^3P) \rightarrow HCCCH(^1A') + H(^2S) \quad (4)$$

we obtain an energy of reaction of −200 kJ/mol, which is 10 kJ/mol more exothermic than at the CCSD(T)/6-311+G(3df,2p) level [105]. In our calculations, the basis-set incompleteness and core–valence correlation corrections amount to −3.4 kJ/mol each.

3.2.9. Triplet prop-2-ynylidene, HCCCH

We locate the ^3B ground state of prop-2-ynylidene 53.8 kJ/mol below the singlet C_s structure (Table 2). This value compares well with the CCSD(T)/6-311 G+(3df,2p) value of Nguyen et al. [105] of 48.1 kJ/mol. In its ground state, prop-2-ynylidene displays C_2 symmetry [105,106,112]. On the triplet potential energy hypersurface calculated at the CCSD(T)/TZP level, [106] stationary points with Hessian index 1 (C_s symmetry) and 2 (C_{2v} symmetry) are found 0.5 and 0.7 kJ/mol, respectively above the C_2 minimum. It is noted, however, that single-point coupled-cluster calculations in the larger QZ2P basis set, carried out at the CCSD(T)/TZP geometries, located the C_s triplet 0.3 kJ/mol below the C_2 structure. At the CASPT2 level, Rubio et al. [112] have found the C_2 structure ca. 0.8 kJ/mol below the C_s structure. Since all of the above energy differences are below 1 kJ/mol, we have decided to concentrate our calculations on the C_2 structure, which is regarded as the global minimum on the triplet surface [105,106,112].

3.2.10. Trans-Propenediylidene, HCCHC

Trans-propenediylidene (*trans* with respect to the H atoms) shows C_s symmetry and is 254 kJ/mol less stable than triplet prop-2-ynylidene (Table 2). This value is consistent with the energy difference of 251 kJ/mol reported by Ochsenfeld et al. [106] at the CCSD(T)/QZ2P level (including ZPVE). Also their C–C bond lengths (134.9 and 139.2 pm) compare well with ours (134.7 and 138.2 pm). Nguyen et al. [105] report a slightly smaller relative energy (246 kJ/mol) from CCSD(T)/6-311+G(3df,2p) single-point calculations at B3LYP/6-311 G(d,p) geometries, in which the C–C bond lengths are 135.4 and 137.4 pm.

3.2.11. Cyclopropene-1,2-diyl, c-CH_2CC

Cyclopropene-1,2-diyl (cyclopropyne) has C_{2v} symmetry (nonplanar, perpendicular structure) and a $^3B_1$ ground state when the C atoms are chosen to lie in the *xz* plane and the H atoms in the *yz* plane [103]. In the CCSD(T)(Full)/cc-pCVQZ′ equilibrium structure, the two equivalent C–C bonds are 156.0 pm and the unique C–C bond is 129.5 pm long. Other researchers have found the corresponding values 155.6/130.0 pm (CISD/DZP), [107] 158.6/131.4 pm (CASSCF), [112] and 156.7/128.9 pm [B3LYP/6-311G(d,p)] [105]. We find triplet cyclopropyne 249 kJ/mol above triplet prop-2-ynylidene, the global minimum on the triplet surface (*vide supra*). This value can be compared with the CCSD(T)/6-311+G(3df,2p) value of Nguyen et al. [105] which amounts to 238 kJ/mol.

3.2.12. 2-Propynyl, CH_2CCH

2-Propynyl (propargyl) is the most stable C_3H_3 isomer on the doublet surface. The planar radical shows C_{2v} symmetry and has a $^2B_1$ ground state (with the molecule in the *yz* plane).

In 1970, Walsh reported an experimental heat of formation of $\Delta_f H^0(298.15\ K) = 360.5 \pm 5$ kJ/mol, [115] which gives $\Delta_r H^0(298.15\ K) = 2443.5$ kJ/mol for the atomization reaction. Correcting for the difference $\Delta_r H^0(298.15\ K) - \Delta_r H^0(0\ K) = 25.2$ kJ/mol, which is estimated from the UHF–CCSD(T)/cc-pCVTZ′ harmonic vibrational frequencies and the experimental electronic energy levels of the C atom, we obtain an experimentally derived estimate for the atomization energy of 2418 ± 5 kJ/mol, in reasonable agreement with our theoretical value (2424 kJ/mol). More recently, Robinson et al. [113] experimentally derived the value $\Delta_f H^0(298.15\ K) = 345 \pm 13$ kJ/mol, which yields an atomization energy of $\sum D_0(0\ K) = 2434 \pm 13$ kJ/mol. The heat of formation of Robinson al. [113] has been confirmed by Harkless and Lester by means of diffusion Monte Carlo (DMC) calculations [116]. These authors report $\Delta_f H^0(298.15\ K) = 345.2 \pm 2.5$ kJ/mol in full agreement with the experimental value of Robinson et al. [113]. However, the two DMC values for the atomization energy of propargyl reported in Ref. [116] (without ZPVE, that is, $\sum D_e = 607.6$ and 608.6 kcal/mol) are ca. 3–4 kcal/mol larger than our value (2530.4 kJ/mol or 604.8 kcal/mol).

Very recently, Wheeler and co-workers [8] reported the theoretically determined value $\Delta_f H^0(0\ K) = 84.76$ kcal/mol (354.6 kJ/mol) with an error not larger than 0.3 kcal/mol. This value translates into an atomization energy of $\sum D_0(0\ K) = 2427 \pm 1$ kJ/mol, only 3 kJ/mol larger than our value. The value of Wheeler et al. [8] was obtained via the reactions

$$CH_2CCH_2(^1A_1) + CH_3(^2A_2'') \rightarrow CH_2CCH(^2B_1) + CH_4(^1A_1) \quad (5)$$

and

$$CH_3CCH(^1A_1) + CH_3(^2A_2'') \rightarrow CH_2CCH(^2B_1) + CH_4(^1A_1) \quad (6)$$

using accurate heats of formation for 1,2-propadiene (allene) and propyne, respectively. Our $\Delta_r H^0(0\ K)$ value for reaction (5) amounts to −57.9 kJ/mol while at the focal-point extrapolated CCSD(T) level of Wheeler et al. the corresponding value is −59.5 kJ/mol. Changing the correlation treatment to the CCSDT(Q) approach (full triples with corrections for quadruples) changed this value by −0.7 kJ/mol to −60.2 kJ/mol [8].

3.2.13. 1-Propynyl, CH_3CC

1-Propynyl exhibits a $^2A_1$ ground state in C_{3v} symmetry. Our calculations locate 1-propynyl 174.0 kJ/mol above 2-propynyl while Nguyen et al. [105] report an energy difference of 168 kJ/mol at the CCSD(T)/6-311+G(3df,2p) level. At the frozen-core CCSD(T) level, without ZPVE and other corrections, the energy difference between 1-propynyl and 2-propynyl amounts to 166.3 kJ/mol in our calculations (with an basis-set incompleteness correction of only 0.3 kJ/mol), whereas Nguyen et al. [105] report 163.4 kJ/mol.

Our value is in agreement with the value reported by Wheeler et al., who obtained $\Delta_r H^0(0\ K) = 175$ kJ/mol for the reaction

$$CH_2CCH(^2B_1) \rightarrow CH_3CC(^2A_1). \quad (7)$$

3.2.14. Cycloprop-1-enyl, c-CH_2CHC

Concerning the reaction

$$C_2H_3(^2A') + C(^3P) \rightarrow c\text{-}CH_2CHC(^2A'). \quad (8)$$

Nguyen et al. report an exothermic energy of reaction (at 0 K) of −111.8 kcal/mol (−468 kJ/mol) at the CCSD(T)/6-311+G(3df,2p) level. We obtain −485 kJ/mol for this reaction energy (cf. Tables 1 and 2). Again, the difference between the two coupled-cluster results can be traced back partly to the basis-set incompleteness and CV corrections (−7.5 and −3.9 kJ/mol) that are taken into account in the present work. Taking the atomization energy (2253 kJ/mol) determined by Wheeler et al. [8] and the ATcT value for the vinyl radical from Table 1 also yields a reaction enthalpy of −485 kJ/mol.

3.2.15. Cycloprop-2-enyl, c-CHCHCH

Nguyen et al. have found the $^2A'$ state of cycloprop-2-enyl at 8.8 kcal/mol (37 kJ/mol) below the $^2A'$ state of cycloprop-1-enyl, in agreement with our results. Table 3 reports a difference between the atomization energies of 36.6 kJ/mol. The value obtained by Wheeler et al. [8] amounts to 37.3 kJ/mol. All of these values mutually agree to within 1 kJ/mol.

3.2.16. Doublet 1-propene-1-yl-3-ylidene, CHCHCH

Le et al. [117] have performed CCSD(T)/6-311G(d,p)//B3LYP/6-311G(d,p) calculations of the reaction

$$C_2H_4(^1A_g) + C(^3P) \rightarrow CHCHCH(^2A'') + H(^2S) \quad (9)$$

and obtained an endothermic reaction energy of 142 kJ/mol (at 0 K, including ZPVE). Our best estimate amounts to 134 kJ/mol.

Table 3
C_3H_3 isomers and 1,2-propadiene: frozen-core (FC) and core–valence (CV) contributions to the equilibrium atomization energy D_e (0 K), harmonic (Harm.) and anharmonic (Anharm.) zero-point vibrational energy contributions E_{ZPVE}, spin–orbit energy contributions E_{SO}, first-order Darwin (Darwin) and mass–velocity (Ms.–Vel.) scalar relativistic energy contributions E_{SR}, and calculated (Calc.) and experimental or previous theoretical (Exptl./Theor.) atomization energy $\sum D_0$ (0 K)

Species	State	D_e (0 K)		E_{ZPVE}		E_{SO}	E_{SR}		$\sum D_0$ (0 K)	
		FC	CV	Harm.	Anharm.		Darwin	Ms.–Vel.	Calc.	Exptl./Theor.
2-Propynyl, CH_2CCH	$^2B_1$	2 519.18[a]	14.18	−106.82	0.73	−1.06	5.53	−7.46	2 424.28	2418 ± 5[b]
										2434 ± 13[c]
										2427 ± 1[d]
1-Propynyl, CH_3CC	$^2A_1$	2 352.87[a]	13.22	−114.73	1.97	−1.06	5.69	−7.70	2 250.26	2252 ± 1[d]
Cycloprop-1-enyl, c-CH_2CHC	$^2A'$	2 354.21[a]	12.45	−112.86	1.53	−1.06	5.40	−7.36	2 252.31	2253 ± 1[d]
Cycloprop-2-enyl, c-CHCHCH	$^2A'$	2 389.48[a]	13.50	−112.48	1.55	−1.06	5.85	−7.95	2 288.88	2291 ± 1[d]
1-Propene-1-yl-3-ylidene	$^2A''$[e,f]	2 182.01[a]	11.34	−101.27	1.52[g]	−1.06	5.31	−7.24	2 090.69	
	$^4B_2$	2 216.26[a]	12.13	−103.19	1.40	−1.06	5.37	−7.31	2 123.61	
2-Propene-1-yl-3-ylidene	$^2A''$[e]	2 315.89[a]	11.00	−107.80	2.13[g]	−1.06	4.42	−6.02	2 218.56	
1,2-Propadiene, CH_2CCH_2	$^1A_1$	2 929.00	14.32	−143.21	1.66	−1.06	5.60	−7.59	2 798.71	2799.3 ± 1.3[h]

All values in kJ/mol.
[a] Valence-shell triples correction (T) computed in the cc-pCVQZ′ basis.
[b] Ref. [115].
[c] Ref. [113].
[d] Ref. [8].
[e] UHF–CCSD(T)/cc-pCVTZ′ optimized geometry.
[f] UHF reference was used.
[g] B97-1/6-31+G** value.
[h] Ref. [94].

3.2.17. Quartet 1-propene-1-yl-3-ylidene, CHCHCH

Vereecken et al. [31] found the $^4B_2$ state of 1-propene-1-yl-3-ylidene about 26 kJ/mol below the doublet state (ZPVE included) at the level of B3LYP-DFT/6-31 G** level. The corresponding value obtained in the present work is 33 kJ/mol.

3.2.18. 2-Propene-1-yl-3-ylidene

The planar 2-propene-1-yl-3-ylidene radical has a $^2A''$ ground state in C_s symmetry. We obtain an exothermic energy of reaction (at 0 K) of −451 kJ/mol for the reaction

$$C_2H_3(^2A') + C(^3P) \rightarrow CH_2CHC(^2A''), \quad (10)$$

whereas Nguyen et al. report −105.0 kcal/mol (−439 kJ/mol) at the CCSD(T)/6-311+G(3df,2p) level.

3.2.19. 1,2-Propadiene, CH_2CCH_2

The experimentally derived atomization energy of 1,2-propadiene (or allene) amounts to 2799.3 ± 1.3 kJ/mol. Our computed value (2798.7 kJ/mol) agrees with this value to within the experimental error bar. The agreement between the calculated and experimental numbers highlights the accuracy of our computational approach based on the CCSD(T)-R12 method. Note, however, that 1,2-propadiene is a simple closed-shell molecule and single-reference case. The accuracy for the radicals and open-shell systems may be somewhat lower.

4. Conclusions

We have performed explicitly-correlated coupled-cluster calculations at the level of CCSD(T)-R12 theory on nineteen molecules and radicals of the type C_3H_x. Spin-restricted Hartree–Fock reference wave functions were used in conjunction with very large basis sets (19s14p8d6f4g3h for C and 9s6p4d3f for H). CCSD-R12 calculations could be carried out with as many as 840 (C_3H_3) or 908 (C_3H_4) basis functions, but the (T) triples correction had to be computed in a smaller quadruple-zeta basis set on a few occasions.

It was demonstrated by similar calculations on selected CH_x and C_2H_x species that the CCSD(T)-R12 approach has the potential to yield very accurate atomization energies. For these species, the calculated atomization energies agreed with the ATcT values to within 1.4 kJ/mol (mean absolute deviation), more or less within chemical accuracy (1 kcal/mol).

The atomization energies presented here may serve as benchmark data for future explicitly-correlated coupled-cluster calculations using STGs in the place of the linear r_{12} terms, as suggested by Ten-no [55]. At the level of CCSD(T) theory, the use of STGs makes possible calculations in (augmented) triple-zeta basis sets that are as accurate as those in (augmented) quintuple-zeta basis sets [56,57]. Hence, much smaller basis sets than those used in the present work may be used and much larger systems may be treated in the future.

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