Equilibrium Geometry of the Ethynyl (CCH) Radical[†]

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The equilibrium geometry of the ethynyl (CCH) radical has been obtained using the results of high-level quantum chemical calculations and the available experimental data. In a purely quantum chemical approach, the best theoretical estimates (1.208 Å for r_{CC} and 1.061−1.063 Å for r_{CH}) have been obtained from CCSD(T), CCSDT, MR-AQCC, and full CI calculations with basis sets up to core-polarized pentuple-zeta quality. In a mixed theoretical−experimental approach, empirical equilibrium geometrical parameters (1.207 Å for r_{CC} and 1.069 Å for r_{CH}) have been obtained from a least-squares fit to the experimental rotational constants of four isotopomers of CCH which have been corrected for vibrational effects using computed vibration-interaction constants. These geometrical parameters lead to a consistent picture with remaining discrepancies between theory and experiment of 0.001 Å for the CC and 0.006−0.008 Å for the CH distances, respectively. The corresponding r_s and r_0 geometries are shown not to be representative for the true equilibrium structure of CCH.

I. Introduction

Considerable effort has been devoted to the determination of the structure of the ethynyl (CCH) radical in its $^2\Sigma^+$ electronic ground state from the experimental[1] and the theoretical side.[2−7] Presently, experimental values for ground-state rotational constants (B_0) for four isotopomers of CCH have been determined. For CCH, a value of 43 674.528 94(115) MHz has been reported by Müller et al.[8] in agreement with earlier measured values.[9−11] For ^{13}CCH and C ^{13}CH, values of 42 077.462(1) and 42 631.382(1) MHz have been obtained by McCarthy et al.[12] in excellent agreement with a previous report of Bogey et al.[1,13] Finally, for the deuterated form CCD, a value of 36 068.0310(96) MHz has been reported by Bogey et al.[14]

On the basis of the available experimental rotational constants, Bogey et al.[1] determined a so-called substitution (r_s) structure. However, the obtained bond distances are not in satisfactory agreement with corresponding calculated equilibrium values;[2−7] in particular, the CH distance was unusually short (1.046 Å vs calculated values of 1.062−1.070 Å). As has been already pointed out by Bogey et al.,[14] the observed discrepancy is probably due to the large amplitude bending motion in CCH which is not adequately accounted for in the substitution approach[15] that provides the r_s structure. Thus, determination of the true equilibrium geometry is necessary to get a reliable picture of the structure of the ethynyl radical.

Although the available rotational constants form a solid basis for the experimental determination of the r_0 and r_s geometry, respectively, there is not enough experimental information available to determine the equilibrium geometry. In particular, the vibrational contributions to the rotational constants, which in principle can be determined via the complete set of vibration−rotation interaction constants,[16] cannot be obtained from the available experimental data.

As has been suggested long ago by Pulay et al.[17] and more recently by others,[18,19] quantum chemical calculations can be used to provide the lacking information. With computed vibration−rotation interaction constants (α_r), it is possible to correct experimental rotation constants for vibrational effects and to obtain the corresponding equilibrium values

$$B_e = B_0 + \frac{1}{2}\sum_r \alpha_r \tag{1}$$

with the sum running over all vibrational degrees of freedom.

The accuracy of such a mixed experimental−theoretical (or empirical) procedure for the determination of equilibrium geometries has recently been investigated by Pawlowski et al.[20] for a set of 18 closed-shell molecules. It was concluded in this study that errors in the determined empirical bond lengths are below 0.001 Å, if the vibrational corrections to the rotational constants are calculated at a sufficiently high level such as the coupled-cluster singles and doubles (CCSD) level[21] augmented by a perturbative treatment of triple excitations (CCSD(T))[22] together with the cc-pVQZ set from Dunning's correlation-consistent basis-set hierarchy.[23] Although it is not clear whether the same accuracy can be achieved for open-shell systems, this combined experimental−theoretical procedure opens an interesting possibility for the determination of a reliable equilibrium geometry for CCH.

Alternatively, accurate equilibrium geometries can be obtained via a purely theoretical approach. Such an approach can and should take advantage of existing hierarchies of methods for the treatment of electron correlation and establish basis-set convergence by using basis-set sequences such as, for example, the correlation-consistent sets developed by Dunning and coworkers.[23,24] As has been shown by Helgaker et al.[25] and more recently also by Bak et al.[26] such a procedure can lead to an accuracy of 0.002−0.003 Å in bond distances if CCSD(T) calculations together with sufficiently large basis sets are carried out. Again, this conclusion is mainly valid for closed-shell

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molecules and needs to be checked for open-shell systems, for which some further complications are expected.[27,28] Concerning the use of multireference methods, a recent study on more than 60 electronic (closed- and open-shell) states of various diatomic molecules found that approaches such as, for example, the multireference-averaged quadratic coupled-cluster (MR-AQCC) method,[29,30] provide bond distances with an accuracy close to 0.001 Å. As multireference methods together with a careful selection of the reference space offer a well-balanced treatment for both open- and closed-shell molecules, such calculations should be considered useful complements to single-reference-based CC calculations.

The aim of the present paper is to provide an accurate equilibrium geometry for the electronic ground state of the ethynyl radical by using both procedures outlined above. The accuracy and reliability of the theoretically determined values will be carefully investigated via benchmark calculations up to the full configuration interaction (FCI) level. Calculated vibrational corrections to the rotational constants are used to derive equilibrium geometrical parameters from the available experimental rotational constants. The accuracy achieved is judged by a comparison of the results obtained with the two procedures.

II. Computational Methods

Theoretical determinations of the equilibrium geometry of CCH have been carried out using various coupled-cluster (CC) approaches and, to investigate possible multireference effects, the multireference configuration interaction (MR-CI) and multireference-averaged quadratic coupled-cluster (MR-AQCC) methods.

Using the CC ansatz, calculations have been performed at two levels beyond the coupled-cluster singles and doubles (CCSD)[21] approximation, namely, at the CCSD(T) level which includes connected triple excitations perturbatively on top of a CCSD calculation[22,31] and at the CCSDT level[32−34] which includes a full treatment of triple excitations. Both unrestricted Hartree−Fock (UHF) and restricted open-shell Hartree−Fock (ROHF) reference functions have been used in the CC calculations.

The MR-AQCC method can be considered an approximately "extensive" version of the MR-CISD (multireference configuration interaction with single and double excitations) method. MR-AQCC and MR-CISD calculations have been carried out with different reference (active) spaces. The n_e factor in the MR-AQCC calculations was chosen to be 9, that is, the core electrons are not considered in the size-extensivity correction (for details, see ref 30).

The hierarchy of correlation-consistent basis sets cc-pVXZ[23] and cc-pCVXZ[24] has been used with X = D,T,Q, and 5.

Since the size of CCH renders FCI calculations with small basis sets possible, FCI calculations (with a restricted open-shell HF reference) have been carried out for the geometry of CCH employing the cc-pVDZ basis sets. These benchmark results are used to calibrate the corresponding CC and MR-AQCC results.

Geometry optimizations have been carried out with analytically evaluated gradients in the case of the CCSD(T)[31,35−37] and MR-AQCC calculations,[38,39] while in all other cases the equilibrium geometry has been determined using purely numerical methods.

The vibration−rotation interaction constants which are needed to subtract the vibrational contribution from the experimental rotational constants have been obtained at the UHF-CCSD(T) and ROHF-CCSD(T) levels using cc-pVTZ, cc-pCVTZ, cc-pVQZ, and cc-pCVQZ basis sets[23,24] at the geometry optimized at the same level. The required quantities (for the relevant computational expressions, see, for example, ref 16) have been determined using analytic derivative techniques, that is, the harmonic force field was determined using either analytic gradients (ROHF-CCSD(T))[31] or analytic second derivatives (UHF-CCSD(T)),[40,41] and the cubic force field has been subsequently determined via numerical differentiation as described in refs 19 and 42. In addition, to check the reliability of the obtained force fields, UHF-CCSDT calculations of the vibration−rotation interaction constants (within the frozen-core approximation) have been carried out employing our recently implemented general CC analytic second derivatives.[43]

CC calculations have been performed with the Austin−Mainz version of the ACES II program system.[44] The COLUMBUS suite of programs[39,45] was used for the MR-AQCC and the LUCIA code[46] for the FCI calculations. The CCSDT force field calculations have been carried using the generalized CI/CC code developed by one of us[47−49] which has been interfaced to the ACES II program.

III. Results and Discussions

III.A. Choice of Reference Space in the Multireference Treatments. The $^2\Sigma^+$ ground state of CCH has a dominant configuration of $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4\ 5\sigma$. An appropriate reference space for the description of this electronic state within a MR-AQCC treatment has to be selected in a careful manner. In the present work, four different reference spaces have been tested with respect to their performance for the equilibrium geometry of CCH. In particular, the convergence of the calculated geometrical parameters with increase of the reference space is investigated.

The smallest reference space is of complete active space (CAS) type and denoted by "5 × 5", indicating that five electrons are distributed within five orbitals, namely the open-shell 5σ, the pairs of the π and π^* orbitals (1π and 2π). The next CAS reference space, denoted by "5 × 6", considers in addition the virtual 6σ orbital, while the largest CAS space ("5 × 8") includes three virtual orbitals (6σ, 7σ, and 8σ). Finally, to investigate the effect of including further "active" electrons, the "5 × 6" space has been augmented by single and double excitations involving the 3σ and/or 4σ orbital (in the following denoted by "5 × 6 + 2d"). Note that in all considered cases, the orbitals have been taken from MCSCF calculations using the same space. All single and double excitations out of the reference configurations have been included in the correlation treatment within the MR-CISD and MR-AQCC calculations. As the focus of these initial calculations is just the convergence of the results with respect to the chosen reference space, the calculations have been performed at the cc-pVDZ and cc-pVTZ basis-set levels, respectively.

TABLE 1: Comparison of Geometrical Parameters (in Å) for the $^2\Sigma^+$ State of CCH with Respect to the Chosen Reference Space in the MR-CISD and MR-AQCC Treatments[a]

	5 × 5	5 × 6	5 × 8	5 × 6 + 2d
	r_{CC}			
MR-AQCC/cc-pVDZ (fc)	1.2369	1.2376	1.2379	1.2371
MR-CISD/cc-pVTZ (ae)	1.2093	1.2102	1.2102	1.2123
MR-AQCC/cc-pVTZ (ae)	1.2121	1.2129	1.2131	1.2126
	r_{CH}			
MR-AQCC/cc-pVDZ (fc)	1.0794	1.0797	1.0807	1.0799
MR-CISD/cc-pVTZ (ae)	1.0546	1.0548	1.0552	1.0558
MR-AQCC/cc-pVTZ (ae)	1.0573	1.0575	1.0580	1.0580

[a] fc = frozen-core calculations, ae = all-electron calculations.

TABLE 2: Comparison of Geometrical Parameters (in Å) for the $^2\Sigma^+$ State of CCH as Obtained at the CCSD(T), CCSDT, and MR-AQCC Levels Using Different Basis Sets[a]

	r_{CC}					r_{CH}				
	UHF-CCSD(T)	ROHF-CCSD(T)	UHF-CCSDT	ROHF-CCSDT	MR-AQCC	UHF-CCSD(T)	ROHF-CCSD(T)	UHF-CCSDT	ROHF-CCSDT	MR-AQCC
cc-pVDZ (fc)	1.2318	1.2353	1.2352	1.2354	1.2376	1.0797	1.0801	1.0801	1.0802	1.0797
cc-pVTZ (fc)	1.2120	1.2153	1.2150	1.2151	1.2173	1.0643	1.0646	1.0645	1.0645	1.0638
cc-pVQZ (fc)	1.2081	1.2113	1.2110	1.2110	1.2133	1.0642	1.0645	1.0644	1.0644	1.0635
cc-pV5Z (fc)	1.2072	1.2104		1.2098	1.2123	1.0639	1.0642		1.0642	1.0632
cc-pCVTZ (ae)	1.2087	1.2119			1.2132	1.0642	1.0645			1.0627
cc-pCVQZ (ae)	1.2052	1.2083			1.2096	1.0630	1.0632			1.0613
cc-pCV5Z (ae)	1.2043	1.2074				1.0626	1.0629			

[a] fc = frozen-core calculations, ae = all-electron calculations. [b] 5 × 6 reference space.

The corresponding results are compiled in Table 1. The most significant observation is that there is a faster convergence of the bond distance with increase of the reference space in the MR-AQCC than in the MR-CISD calculations, as the MR-AQCC results seem to be much less sensitive to the choice of reference space. While the optimized bond distances obtained with the two methods are very close when the largest reference space (5 × 6 + 2d) is used, there are noticeable differences for the smaller reference spaces. For these, the MR-AQCC results are much closer to the "5 × 6 + 2d" values than the corresponding MR-CISD results. In particular, the inclusion of additional electrons in the reference space seems to be less important when using the MR-AQCC ansatz. The results in Table 1 thus indicate that the use of a "5 × 6" active space seems to be a safe and economical choice for large-scale MR-AQCC calculations on the $^2\Sigma^+$ state of CCH. The remaining error due to higher excitations is estimated to be about 0.001−0.002 Å.

III.B. Comparison of MR-AQCC and CC Results. In Table 2 the CC and CH bond lengths obtained at CCSD(T), CCSDT, and MR-AQCC levels using different basis sets are compared.

Focusing first on the coupled-cluster results, it is observed that, independent of the chosen basis set, the CC distances obtained at the UHF-CCSD(T) level are about 0.003 Å shorter than the corresponding CCSDT values, while the corresponding ROHF-CCSD(T) bond lengths are essentially identical to both the UHF- and ROHF-CCSDT values. This unexpected difference between the UHF and ROHF results is investigated in a forthcoming article[28] where the failure of UHF-CCSD(T) is traced back to a rapid change of the underlying UHF wave function at certain bond distances. It will be shown in ref 28 that this breakdown of the UHF-CCSD(T) approach occurs for the ethynyl radical at distances close to the equilibrium geometry, and thus, the UHF-CCSD(T) results must be considered unreliable. Interestingly, the full CCSDT approach seems to be able to recover from these deficiencies of the underlying UHF reference functions and provides results which are essentially independent of the chosen reference functions.

For the CC distances the differences between ROHF-CCSD(T) and CCSDT are essentially negligible. When considering in addition the MR-AQCC calculations (obtained with the "5 × 6" reference), we note that the MR-AQCC value for the CC distance is even longer than the corresponding CCSDT value (by about 0.002 Å). It is essentially impossible at this point to decide whether the CCSDT or the MR-AQCC results should be considered more accurate.[50] Good agreement of the ROHF-CCSD(T) and CCSDT also suggests that ROHF-CCSD(T) can be safely used with the larger basis sets where CCSDT is not practical.

For the CH distance, all considered approaches yield essentially the same result.

TABLE 3: Comparison of Geometrical Parameters (in Å) for the $^2\Sigma^+$ State of CCH at the CCSD(T), CCSDT, and MR-AQCC Levels with Corresponding FCI Calculations[a]

	r_{CC}	r_{CH}
ROHF-CCSD(T)	1.2353	1.0801
UHF-CCSD(T)	1.2318	1.0797
UHF-CCSDT	1.2352	1.0801
ROHF-CCSDT	1.2354	1.0802
MR-AQCC[b]	1.2376	1.0797
FCI	1.2367	1.0802

[a] All calculations with cc-pVDZ and core orbitals frozen in the electron-correlation treatment. [b] 5 × 6 reference space.

III.C. Comparison with Full Configuration Interaction Results. To judge the accuracy of MR-AQCC and CCSDT, benchmark calculations at the FCI level using the cc-pVDZ basis have been performed. The corresponding results are summarized in Table 3. As these results show, the CH bond distances obtained by any approach are in excellent agreement (differences are less than 0.0005 Å), while for the CC bond distance the FCI result falls between the corresponding CCSDT and MR-AQCC values. This means that in comparison with FCI the CCSDT value is about 0.001 Å too short, while MR-AQCC is about 0.001 Å too long. Both methods thus exhibit errors which are acceptable for our purpose.

III.D. Basis-Set Convergence. After discussing the issue of electron correlation, we will now turn our interest to the basis-set effects. Results obtained with both the cc-pVXZ and cc-pCVXZ sequence of basis sets have been given in Table 2. In the cc-pVXZ calculations, when employing the frozen-core approximation, smooth convergence of the geometrical parameters is observed. When going from cc-pVDZ to cc-pV5Z, both bond distances are reduced, the CC distance by about 0.025 Å and the CH distance by about 0.016 Å. The differences between the cc-pVQZ and cc-pV5Z results are with 0.001 and 0.0003 Å already rather small so that the cc-pV5Z results can be considered as nearly converged. However, the cc-pVXZ calculations do not incorporate core-correlation effects. To consider these properly, all-electron calculations using the core-valence correlating cc-pCVXZ sets have been carried out. As for the cc-pVXZ sequence, monotonic convergence is observed for the geometrical parameters within this basis-set sequence and the differences between quadruple- and pentuple-zeta results are again small. From the results, it is further seen that core correlation together with the additional consideration of core polarization functions reduces the CC bond distance by about 0.003−0.004 Å, while the CH distance, as one might expect, is less affected and shortened by only 0.001−0.002 Å.

Unfortunately, because of program limitations, it was not possible to perform MR-AQCC calculations using the largest cc-pCV5Z basis. However, the rather systematic difference between the CCSD(T) and MR-AQCC results enables a

TABLE 4: Calculated Vibrational Corrections $\Delta B = B_e - B_0$ (in MHz) to the Rotational Constants of Different Isotopomers of CCH from UHF- and ROHF-based CC Calculations

	CCSD(T) cc-pVTZ	CCSD(T) cc-pVQZ	CCSD(T) cc-pCVTZ	CCSD(T) cc-pCVQZ	CCSDT(fc) cc-pVTZ[a]
UHF Reference Function					
CCH	368.27	334.70	379.67	355.74	583.64
^{13}CCH	355.08	322.65	366.09	342.76	564.26
C^{13}CH	366.25	333.16	377.31	353.24	580.54
CCD	168.07	151.12	175.33	167.52	258.47
ROHF Reference Function					
CCH	531.16	479.58	568.24	495.37	
^{13}CCH	513.21	463.24	549.12	478.15	
C^{13}CH	528.13	476.98	564.57	491.72	
CCD	237.85	214.59	257.20	230.11	

[a] fc = frozen-core calculation.

prediction of the corresponding value based on MR-AQCC/cc-pCVQZ and ROHF-CCSD(T)/cc-pCV5Z calculations. As the use of the pentuple- instead of the quadruple-ζ set decreases CC and CH bond distances by about 0.0009 and 0.0004 Å, respectively, the estimated MR-AQCC/cc-pCV5Z values are about 1.2087 and 1.0609 Å.

The influence of diffuse functions has been investigated at the UHF-CCSD(T) level. It was found that the changes amounts to less than 0.0003 Å when going from cc-pCVQZ to aug-cc-pCVQZ.

III.E. Best Theoretical Estimates. On the basis of the previous sections, we are now able to give a best theoretical estimate for the equilibrium geometry of CCH. There are two (almost) independent procedures: one uses the MR-AQCC data while the other uses the CC data, respectively. At the MR-AQCC level, the best directly calculated geometry has been obtained with cc-pCVQZ basis set (r_e(CC) = 1.2096 Å and r_e(CH) = 1.0613 Å). This geometry should be "improved" by the FCI correction obtained at the cc-pVDZ level, that is, by −0.0009 and 0.0005 Å as well as corrected for the remaining basis-set effect, that is, by −0.0009 Å and −0.0004 Å, for CC and CH, respectively (see above). Assuming additivity of these corrections, this leads to final values of 1.2078 and 1.0614 Å for the CC and CH bond distance, respectively. A similar extrapolation procedure starting from the ROHF-CCSD(T)/cc-pCV5Z results (1.2074 and 1.0628 Å) and employing corrections due to full CCSDT (−0.0003 Å and −0.0001 Å) and FCI (0.0013 and 0.0000 Å) leads to a final estimate of 1.2084 and 1.0627 Å for the two distances. The discrepancy of 0.001 to 0.002 Å between the values obtained with these two extrapolation schemes is an indication for the accuracy of our theoretical results.

It is noteworthy to mention that our best theoretical estimates are in excellent agreement with recent recommendations for the equilibrium geometry of CCH by Peterson and Dunning[7] based on CCSD(T) calculations. The corresponding values are 1.2076 and 1.0619 Å.

III.F. Analysis of Experimental Rotational Constants. After establishing a theoretical estimate for the equilibrium geometry of CCH, we now focus on the analysis of the experimental rotation constants using computed vibrational corrections. These corrections to B, that is, $\Delta B = B_e - B_0$, have been obtained at the UHF- and ROHF-CCSD(T) level using the cc-pVXZ and cc-pCVXZ sets with X = T and Q. The calculated ΔB values are compiled in Table 4 and amount to about 150−590 MHz, that is, about 0.5 to 1.5% of the values of the corresponding rotational constants for the considered isotopomer and thus are non-negligible. However, large discrepancies are seen between the vibrational corrections computed with UHF and ROHF reference functions. We thus decided to check the reliability of the CCSD(T) force fields via corresponding CCSDT calculations using the cc-pVTZ basis set. As is seen from Table 4, the CCSDT calculations suggest that the UHF-CCSD(T) force fields (as the corresponding geometries) should be considered unreliable and that only the ROHF-CCSD(T) approach yields vibrational corrections in good agreement with the CCSDT approach. On the basis of these calculations, we refrain from discussing the UHF-CCSD(T) results any further and solely discuss the corresponding ROHF-CCSD(T) results in the following.

For the least-squares fit of the geometrical parameters to the rotational constants, the most recent B_0 values from refs 8, 12, and 14, as given in the Introduction, have been used together with the vibrational corrections compiled in Table 4. The resulting *empirical* equilibrium geometries are summarized in Table 5. According to the values reported there, an "empirical" equilibrium geometry of r_{CC} = 1.207 Å and r_{CH} = 1.069 Å can be given with 0.002 Å as a conservative error estimate[51] based on the convergence of the results.

A comparison of the empirical equilibrium geometry with our best theoretical estimates shows that the remaining discrepancies are in the range of 0.001 to 0.002 Å for the CC and 0.006 to 0.008 Å for the CH distances. It appears that the empirical value for the CC distance is slightly shorter and the CH distance is longer than the corresponding theoretical values. While these discrepancies can possibly be traced back to remaining deficiencies in the theoretical treatment, another, and maybe more likely, possibility is that these differences point to so far unexplored limitations in the perturbational treatment of the vibrational corrections (note that there is a low-lying Π state which interacts with the electronic ground state through the bending motion).

Nevertheless, the current study leads to a satisfactory agreement between theory and experiment and thus provides a consistent picture with respect to the equilibrium geometry.

Concerning previous efforts to determine the geometry of CCH, we note that the r_s (as well as the r_0) structures are rather

TABLE 5: Comparison of Geometrical Parameters (in Å) for the $^2\Sigma^+$ State of CCH Obtained from Theory and Experiment

structure	r_{CC}	r_{CH}	method	ref
r_e	1.2064	1.0678	from exptl B_0 with ΔB(ROHF-CCSD(T)/cc-pVTZ)	this work
r_e	1.2076	1.0657	from exptl B_0 with ΔB(ROHF-CCSD(T)/cc-pVQZ)	this work
r_e	1.2056	1.0689	from exptl B_0 with ΔB(ROHF-CCSD(T)/cc-pCVTZ)	this work
r_e	1.2075	1.0651	from exptl B_0 with ΔB(ROHF-CCSD(T)/cc-pCVQZ)	this work
r_e	1.2050	1.0703	from exptl B_0 with ΔB(UHF-CCSDT(fc)/cc-pVTZ)	this work
r_e	1.2078	1.0614	est from MR-AQCC	this work
r_e	1.2084	1.0627	est from CCSDT	this work
r_0	1.2193	1.0457	from exptl B_0	this work
r_s	1.21652	1.04653	from exptl B_0	1
r_e	1.2076	1.0619	est from CCSD(T)	7

different (compare Table 5). Both of them deviate by about 0.005 Å in the CC and by about 0.015 Å in the CH distance from the equilibrium geometries obtained in this work. Apparently, unlike often claimed, the substitution approach leading to the r_s structure is not able to eliminate vibrational effects in the case of CCH, and thus, the r_s and r_0 structure turn out to be very similar. Our observation supports the speculation in ref 1 that the significantly too short CH distance is due to insufficient account of vibrational effects, and in particular of the low-frequency bending motion, a well-known artifact of the substitution approach to molecular structures.

IV. Conclusions

Equilibrium geometrical parameters for the $^2\Sigma^+$ state of the ethynyl radical have been obtained using two approaches. The first purely theoretical procedure based on extensive CC, MR-AQCC, and FCI calculations yields values of 1.208 Å for the CC distance and 1.061−1.063 Å for the CH distance, while the second approach based on the analysis of experimental rotational constants using computed vibrational corrections provides values of 1.207 and 1.069 Å. The observed differences between the two approaches of 0.001−0.002 Å for CC and 0.006−0.008 Å for CH are somewhat larger than expected. Among possible causes for this discrepancy, we consider limitations in the perturbational treatment of the vibrational corrections to the rotational constants. The r_s and r_0 geometries for CCH are, because of a missing or insufficient treatment of these corrections, far away from the true equilibrium geometry.

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(50) It should be mentioned here that our MR-AQCC results are in excellent agreement with previous MR-CI calculations by Peterson and Dunning.[7] Their best values at the MR-CI level (augmented by a Davidson correction) using a full valence active space using a pV5Z basis for carbon and a pVQZ basis for hydrogen of 1.2116 and 1.0643 Å are of comparable quality as our MR-AQCC/pV5Z(fc) values of 1.2123 and 1.0632 Å.

(51) Note that the residuals in the least-squares fit were in all cases smaller than 1.5 MHz.