Theor Chim Acta (1993) 86: 97–113

Theoretica Chimica Acta

Low-lying triplet electronic states of acetylene: *cis* $^3B_2$ and $^3A_2$, *trans* ^3B_u and ^3A_u

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Received June 8, 1992/Accepted September 23, 1992

Summary. *Ab initio* molecular electronic structure theory has been used in conjunction with flexible basis sets to investigate the equilibrium properties of the four low-lying triplet electronic states of acetylene. Self-consistent-field (SCF) and configuration interaction with single and double excitations (CISD) levels of theory were employed with basis sets ranging from double zeta plus polarization (DZP) to quadruple zeta plus triple polarization with higher angular momentum polarization functions [QZ(3df, 3pd)]. Complete geometry optimizations of the equilibrium structures and vibrational analyses for the $^3B_2$, ^3B_u, ^3A_u, and $^3A_2$ states as well as the ground $^1\Sigma_g^+$ state of acetylene were carried out at the SCF and CISD levels of theory. With the DZP basis set, configuration interaction with single, double, and triple excitations (CISDT) wavefunctions were also used to optimize geometries. At the CISD optimized geometries the total energies were determined using the correlated wavefunctions with higher excitations. Those wavefunctions include the triple zeta plus double polarization (TZ2P)-CISDT, coupled cluster with single and double excitations (CCSD), and CCSD with perturbative triple excitations [CCSD(T)] methods. Although the energy ordering of $^3B_2 < {}^3B_u < {}^3A_u < {}^3A_2$ remained unchanged, the excitation energies of these four triplet states relative to the $^1\Sigma_g^+$ ground state is increased by about 7.5 kcal/mol in comparison with previous theoretical work. At the highest level of theory, CCSD(T) with the QZ(3df, 3pd) basis set, the classical excitation energies of the four triplet states relative to the ground state were predicted to be 88.0(3.82; 30,790), 96.0(4.16; 33,590), 102.4(4.44; 35,830), and 109(4.76; 38,420) kcal/mol(eV; cm^{-1}), respectively. For the first two triplet states, including the zero-point vibrational energies (ZPVE) the energy differences were 86.6(3.75; 30,270) and 94.8(4.11; 33,170) kcal/mol(eV; cm^{-1}), respectively. The classical energy separation between the $^3B_2$ and $^3A_2$ states was predicted to be 7630 cm^{-1}. Including the estimated ZPVE correction of 50 cm^{-1} this energy difference became 7680 cm^{-1}, which is in very good agreement with the experimental value of 7388 cm^{-1}. The *trans* triplet states have never been observed in the laboratory, and it is hoped that these quantitative theoretical predictions will assist in their experimental identification.

Key words: Acetylene – Low-lying triplet electronic states

1. Introduction

Along with ammonia and formaldehyde, acetylene is one of the three tetra-atomic molecules most exhaustively characterized by spectroscopic techniques. A survey of the experimental spectroscopic literature for acetylene [1–28] for the years 1989–1991 quickly establishes this point. Most of the recent spectroscopic studies [1, 2, 5, 6, 11–13, 15–19, 23, 25, 27] of acetylene have been exclusively concerned with the $^1\Sigma_g^+$ electronic ground state. However, quite a number [3, 4, 7–9, 14, 21, 22, 24, 26] of recent studies have examined the *trans* $\tilde{A}\,^1A_u$ state, the first excited singlet state of acetylene. Despite abundant evidence for the existence of low-lying triplet electronic states of acetylene, only one experimental paper [28] during the past three years addressed this important subject.

Everything that is definitely known about the triplet electronic states of acetylene is the result of a positive interaction between theory and experiment. Theory [29] predicted unequivocally in 1978 that the lowest excited state of acetylene is the *cis* bent $^3B_2$ state. This prediction was confirmed within a year by the work of Wendt, Hippler, and Hunziker [30]. Hunziker and coworkers observed the $^3B_2$–$^3A_2$ electronic transition and found adiabatic energy differences 7388 cm^{-1} for C_2H_2 and 7406 cm^{-1} for C_2D_2. They were also able to determine the quantity $A_0 - (B_0 + C_0)/2$ for both the $^3B_2$ and $^3A_2$ electronic states of C_2H_2 and C_2D_2. Wendt, Hippler, and Hunziker [30] concluded that their experimental results "agree remarkably well with *ab initio* theoretical predictions".

Interestingly, the electronic excitation energy ΔE ($\tilde{X}\,^1\Sigma_g^+ - \tilde{a}\,^3B_2$) has not yet been determined in the laboratory. Neither has there been an experimental assignment of any observed spectroscopic feature that might be due to the predicted [29] low-lying *trans* ^3A_u and ^3B_u electronic states. Since the appearance of the important 1978 theoretical study [29] there has been just one other high level theoretical study of the triplet electronic states of acetylene, namely the 1986 paper by Lischka and Karpfen [31]. The purpose of the present paper is to report a state-of-the-art theoretical study of the four lowest triplet states of acetylene, with reasonable anticipation [28] that further experimental work will be forthcoming shortly.

2. Electronic structure considerations

The ground $\tilde{X}\,^1\Sigma_g^+$ state of acetylene is qualitatively described by the electron configuration:

$$[core](2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4. \tag{1}$$

As is well known the carbon-carbon bond is a typical triple bond, consisting of one σ bond and two π bonds. The highest occupied molecular orbital (HOMO) of the ground state is π bonding (π^b), the $1\pi_u$ orbital, while the lowest unoccupied molecular orbital (LUMO) is antibonding (π^*), the $1\pi_g$ orbital. The degenerate π^b orbital splits into $4a_1$ and $1b_1$ orbitals in C_{2v} symmetry and $3b_u$ and $1a_u$ orbitals in C_{2h} symmetry. On the other hand the degenerate π^* orbital separates into $1a_2$ and $3b_2$ orbitals in C_{2v} symmetry and $1b_g$ and $4a_g$ orbitals in C_{2h} symmetry. A single electronic excitation of the ground state acetylene, from HOMO to LUMO:

$$(1\pi_u)^4 \rightarrow (1\pi_u)^3(1\pi_g) \tag{2}$$

leads to the four low-lying triplet states considered in this paper. As the Walsh diagram [32] indicates and earlier experimental [30] and theoretical [29, 31, 33–36] studies confirmed, these four electronic states have bent structures. The lowest triplet state has a *cis*-bent structure with C_{2v} symmetry and the electron configuration for this $\tilde{a}\ ^3B_2$ state is:

$$[core](2a_1)^2(2b_2)^2(3a_1)^2(1b_1)^2(4a_1)(3b_2). \tag{3}$$

The two open-shell orbitals are oriented in the molecular plane. The second triplet state, $\tilde{b}\ ^3B_u$, has a *trans*-bent structure with C_{2h} symmetry and electron configuration given by:

$$[core](2a_g)^2(2b_u)^2(3a_g)^2(1a_u)^2(3b_u)(4a_g). \tag{4}$$

The two singly occupied electrons are again in orbitals oriented in the molecular plane. The third triplet state considered in this study is the $\tilde{c}\ ^3A_u$ state and is described by:

$$[core](2a_g)^2(2b_u)^2(3a_g)^2(3b_u)^2(1a_u)(4a_g). \tag{5}$$

This electronic configuration may be regarded as a singly excited state relative to either the ground state or the ^3B_u state:

$$\ldots(1a_u)^2(3b_u)(4a_g) \rightarrow \ldots(1a_u)(3b_u)^2(4a_g). \tag{6}$$

In this state one open-shell orbital is directed out-of-plane and the other open-shell orbital is oriented in the molecular plane. The fourth and final triplet state, the $\tilde{d}\ ^3A_2$ state is represented as:

$$[core](2a_1)^2(2b_2)^2(3a_1)^2(4a_1)^2(1b_1)(3b_2). \tag{7}$$

One singly occupied MO is out-of-plane and the other singly occupied electron is in the orbital oriented in the molecular plane. This electronic structure may be alternatively constructed as a single excitation from the $^3B_2$ state:

$$\ldots(1b_1)^2(4a_1)(3b_2) \rightarrow \ldots(1b_1)(4a_1)^2(3b_2). \tag{8}$$

In all four triplet states the carbon-carbon connection consists of one σ bond, one and a half π^b bonds and one-half of a π^* bond. Thus we expect the carbon-carbon linkage of these four triplet states to exhibit double bond characteristics.

3. Stability of the SCF wavefunctions

The four low-lying triplet states, $^3B_2$, ^3B_u, ^3A_u, and $^3A_2$, were investigated in this study. When the molecular frame is maintained in C_{2v} symmetry for *cis*-isomers and in C_{2h} symmetry for *trans*-isomers, the self-consistent field (SCF) wavefunctions for the four triplet states are spatially orthogonal to each other. Thus the total energies of all four triplet states may be obtained in a rigorously variational manner. In the geometry optimization procedure only totally symmetric geometrical parameters need to be considered. The equilibrium structures of the four triplet states, therefore, may be determined within the context of the variation principle. Using similar reasoning, a totally symmetric perturbation of the molecular frame by a small amount does not threaten the orthogonality of the wavefunctions. The physical properties which fall in the totally symmetric irreducible representation, e.g. a_1 (for C_{2v} symmetry) or a_g (for C_{2h} symmetry) components of dipole moment derivatives and harmonic vibrational frequencies, in principle should be correctly determined using SCF methods.

However, if the molecular frame is distorted from the C_{2v} or C_{2h} point group symmetry, the wavefunctions of the upper states may no longer be orthogonal to those of the lower states. In such cases interpretation of the physical properties from the SCF wavefunctions must be carried out with great caution.

In order to examine the stability of the SCF wavefunctions this laboratory has produced a working version of the MO Hessian technique [37]. The MO Hessian may be defined as the second derivative of the total energy with respect to the changes of the MO coefficients. At this point is it useful to introduce the term "instability index" in order to characterize the SCF wavefunction. The instability index is defined as the number of negative eigenvalues for the MO Hessian matrix and is obtained by diagonalizing the MO Hessian matrix constructed at the equilibrium geometry for each triplet state. A wavefunction with non-zero instability index is regarded as "unstable". The eigenvector associated with a negative eigenvalue indicates MO rotations that lower the total energy of the system.

At the given optimized geometry the instability indices are found to be zero for the SCF wavefunctions of the two lower triplet states ($^3B_2$ and ^3B_u), i.e., there are no negative eigenvalues. Thus qualitatively correct dipole moments, dipole moment derivatives and harmonic vibrational frequencies for these two triplet states may be determined at the SCF level.

On the other hand, the two upper states (^3A_u and $^3A_2$) each produce two negative eigenvalues for the MO Hessian matrix, resulting in instability indices of two. Consequently, a careful treatment of physical properties that involve the MO rotations related to these negative eigenvalues is necessary for these higher states [37, 38]. Specifically, the symmetries of the normal modes that involve those MO rotations [38] (with negative eigenvalues) are the a_u and b_u species for the ^3A_u state, but the b_1 and b_2 species for the $^3A_2$ state.

In the current study the CISD (configuration interaction including all single and double excitations) wavefunctions were constructed using the SCF wavefunctions as reference functions. Thus the validity of the CISD wavefunctions is closely related to the orthogonality and stability of the SCF wavefunctions. In general physical properties should be determined correctly via the CISD method as long as the reference wavefunction is orthogonal to all lower-lying electronic state(s). However, when the reference wavefunction is not orthogonal to any lower-lying state or it is unstable, the physical properties determined from the CISD wavefunction may be dubious and should be treated with great care.

4. Theoretical procedures

Five basis sets were employed in this study. The double zeta part of our first basis set was the standard Huzinaga–Dunning double-zeta set of contracted Gaussian functions [39, 40], designated ($9s5p/4s2p$) for C and ($4s/2s$) for H. Our first basis set, the double-zeta plus polarization (DZP) set, was constructed from the DZ set augmented by a single set of d-like polarization functions for C and p functions for H with exponents $\alpha_d(\mathrm{C}) = 0.75$ and $\alpha_p(\mathrm{H}) = 0.75$. The more flexible basis set of triple-zeta plus double-polarization (TZ2P) quality involves Dunning's [41] ($5s3p$) contraction of Huzinaga's [39] ($10s6p$) primitive set of Gaussian functions for C and Dunning's ($3s$) contraction of Huzinaga's ($5s$) set for H augmented with two sets of polarization functions for each atom with orbital exponents $\alpha_d(\mathrm{C}) = 1.50, 0.375$ and $\alpha_p(\mathrm{H}) = 1.50, 0.375$. The third basis set consists of a quadruple zeta contraction of Van Duijneveldt's [42] ($11s7p/6s4p$) set for C and ($7s/4s$) set for hydrogen with the addition of three sets of polarization functions $\alpha_d(\mathrm{C}) = 3.0, 0.75, 0.1875$ and $\alpha_p(\mathrm{H}) = 3.0, 0.75, 0.1875$ and is designated as QZ3P. The fourth and fifth basis sets are the TZ2P and QZ3P basis sets supplemented with higher angular momentum polarization functions $\alpha_f(\mathrm{C}) = 0.8$ and $\alpha_d(\mathrm{H}) = 1.0$, and they are termed TZ(2df, 2pd) and QZ(3df, 3pd), respectively. Sets of six cartesian *d*-like functions and ten cartesian *f*-like functions were used throughout.

All the molecular structures considered for the ground state and triplet states of acetylene have been completely optimized within the given symmetry constraints employing restricted Hartree–Fock (RHF) SCF [43, 44] and configuration interaction (CI) [45, 46] analytic gradient techniques. Residual cartesian and internal coordinate gradients are in all cases less than 10^{-6} atomic units. The quadratic force constants were evaluated using analytic second derivative procedures for the SCF [47, 48] wavefunctions and finite differences of analytic gradients for the CISD wavefunctions.

Electron correlation effects were included by employing the configuration interaction (CI) and coupled cluster (CC) methods. Only the valence electrons were explicitly correlated; thus the two lowest occupied (C 1*s*-like) molecular orbitals were held double occupied (frozen cores) and the two highest lying virtual (C 1*s**-like) orbitals were excluded (deleted virtuals) from the CI and CC procedures. Otherwise, all single and double excitations from the SCF reference configuration were included (CISD and CCSD). With the TZ(2df, 2pd) and QZ(3df, 3pd) basis sets the CISD wavefunctions for the $^3B_2$ state in C_{2v} symmetry involved 38,395 and 64,935 configurations, respectively, in the Hartree–Fock interacting space [49, 50]. These CISD wavefunctions were determined via the shape driven graphical unitary group approach [51]. The contributions from unlinked cluster quadruple excitations to the CISD energies were estimated using the Davidson correction [52, 53], and results incorporating this appendage are denoted CISD + Q.

With the DZP and TZ2P basis sets only, configuration interaction with all single, double and triple excitations (CISDT) wavefunctions were also employed. With these two basis sets the CISDT wavefunctions for the $^3B_2$ state in C_{2v} symmetry involved 520,743 and 3,368,149 all-spin-eigenfunction configurations, respectively. These CISDT wavefunctions are highly unconventional and were constructed via the loop driven graphical unitary group approach [54]. The geometries were optimized for all species with the DZP basis set and only for the ground state with TZ2P basis set. With the TZ2P basis set the energies for the triplet states were evaluated at the CISD optimized geometries.

The first CC method employed was the closed-shell single and double excitation (CCSD) approach of Purvis and Bartlett [55], as was modified by Scuseria and Janssen [56]. The open-shell CCSD wavefunctions were constructed using the methods developed by Scuseria [57]. Connected triple excitations were included using the higher level CCSD(T) method originally proposed by Raghavachari, Trucks, Pople, and Head-Gordon [58]. The CCSD(T) methods actually used were those of Scuseria and Lee [59] for the ground state and Scuseria [57] for the triplet states of acetylene. The energies were determined at the CISD optimized geometries with the corresponding basis set.

5. Results and discussion

Although the ground state of acetylene has been intensively studied theoretically, results for geometry and harmonic vibrational frequencies are reiterated here in order to demonstrate the accuracy and reliability of the analogous wavefunctions used for the excited triplet states.

5.1. Geometries

The optimized geometries of the five equilibrium structures located in this study are presented in Figs. 1–3.

5.1.1. $\tilde{X}^1\Sigma_g^+$ *ground state.* The C–C and C–H bond lengths do not change significantly for both SCF and CISD wavefunctions with basis sets larger than TZ2P. The DZP-SCF wavefunction overestimates the C–H bond length, while the DZP-CISD and DZP-CISDT levels of theory overestimate both the C–C and C–H bond lengths. Note that the largest overestimation is observed for the DZP-CISDT method, which does not represent a good balance between theoretical method (very high level) and basis set (routine). With the larger than DZP basis sets used in this study all wavefunctions underestimate the two bond lengths. With the largest basis set QZ(3df, 3pd), the differences between the predicted and experimental [60] values are 0.0236 and 0.0064 Å at the SCF level, respectively, while they are 0.0084 and 0.0020 Å at the CISD level of theory. At the TZ2P-CISDT level of theory a further improvement is observed. That is, the difference for two bond lengths are only 0.0041 and 0.0017 Å. The good agreement with experiment for the ground state by the CISD and CISDT wavefunctions suggests the reliability of the geometries for the triplet states determined by the same levels of sophistication. However, it is important to realize that a basis set larger than the DZP is required to predict bond lengths within an accuracy of 0.01 Å or better, especially when higher excitations (more than single and double) are included in the configuration interaction space.

5.1.2. Triplet states. An excitation of one electron from a π^b orbital to a π^* orbital in Eq. (2) inevitably increases the C–C bond length. For all four of the triplet states studied in the present research the C–C bond lengths are larger than that for the ground state, as seen in Figs. 2 and 3. With the largest basis set, QZ(3df, 3pd), the C–C bond lengths for the triplet states are predicted to be 1.312–1.351 at the SCF level and 1.325–1.368 Å at the CISD level of theory,

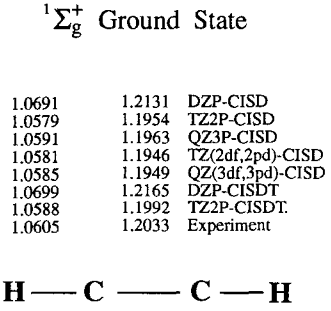

Fig. 1. Predicted equilibrium geometry for the ground-state acetylene at the CISD and CISDT levels of theory. Bond lengths are in Å. Experimental values are from [60]

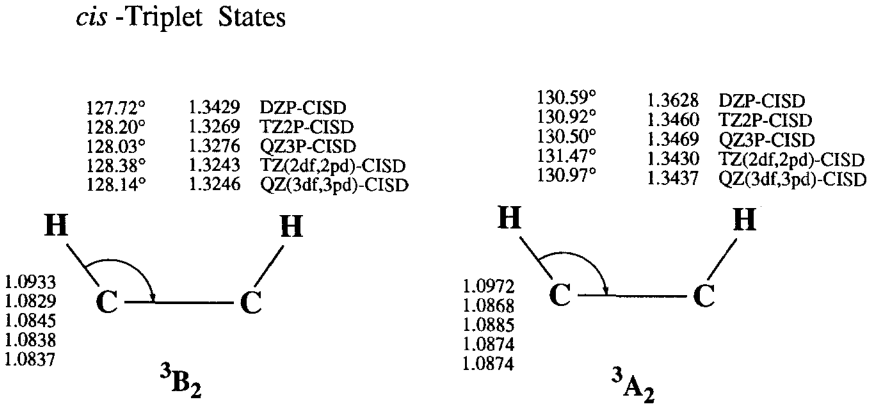

Fig. 2. Predicted equilibrium geometries for the two lowest *cis* triplet states of acetylene at the CISD level of theory. Bond lengths are in Å and bond angles are in degrees

ranges that fall within the category of a C–C double bond. The equilibrium C–C bond length for the prototypical ethylene molecule is experimentally determined to be 1.330 Å [61]. The triplet acetylene C–C bond lengths are smaller for $^3B_2$ and ^3B_u states than those for the ^3A_u and $^3A_2$ states. For the two ^3B states the two open-shell electrons are located in the π^b and π^* orbitals that are both in the molecular plane. On the other hand for the ^3A state one electron stays in an out-of-plane π^b orbital and the other electron resides in the in-plane π^* orbital. Since there are fewer valence electrons involved in the molecular plane for the ^3B states (8 electrons) than for the ^3A states (9 electrons), energetic and structural changes upon electronic excitation are less extensive for the former states. Also it may be reasonable to mention that the carbon atoms in the ^3B states have larger s character than those of the ^3A states. Alternative explanations for the energy ordering of the four triplet states may be seen elsewhere [31, 33–35, 62].

The C–H bond lengths of all four triplet states are larger than the corresponding value for the ground state, consistent with the decrease in bond order of the adjacent carbon-carbon bond. With the largest basis set, the C–H bond lengths for the triplet states are predicted to be 1.072–1.080 Å at the SCF level and 1.077–1.087 Å at the CISD level of theory. Since the experimental C–H bond length for ground state C_2H_4 is 1.076 Å [61], the predicted C–H bond lengths for the triplet states are typical of those adjacent to C–C double bonds. Elongation of the C–H bond length is very likely due to the decrease in the carbon atom s character upon electronic excitation. The ^3A states, for which the carbon atoms have a smaller s character, indeed have longer C–H bond lengths than the ^3B states.

The CCH bond angles for the four triplet states studied here are predicted to be 123.5–132.7° at the SCF level and 121.7–131.4° at the CISD level of theory, using the QZ(3df, 3pd) basis set. The CCH bond angle is smallest for the ^3A_u state. With that basis set it is 123.5° at the SCF and 121.7° at the CISD level of theory, whereas the experimental CCH bond angle for the classically double bonded C_2H_4 molecule is 121.7° [61]. This ^3A_u state has the largest C–C bond length of the four low-lying triplet states and seems to have a typical CCH bond angle involving C–C double bonds.

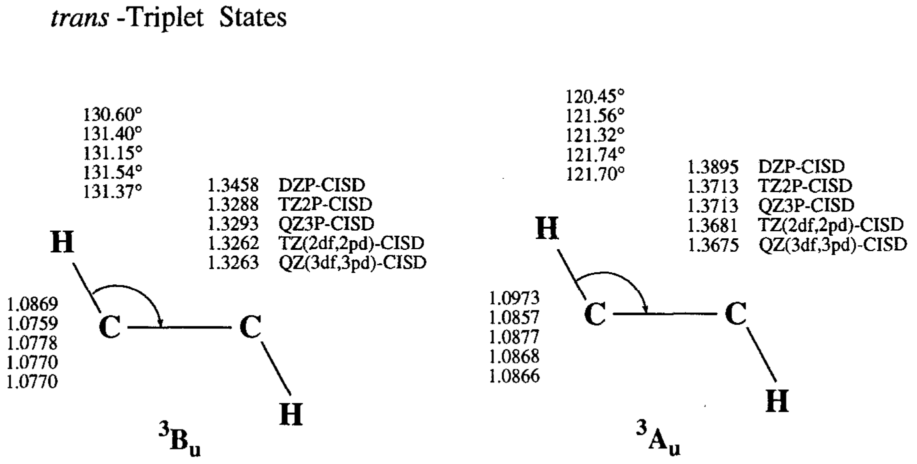

Fig. 3. Predicted equilibrium geometries for the two lowest *trans* triplet states of acetylene at the CISD level of theory. Bond lengths are in Å and bond angles are in degrees

5.2. Harmonic vibrational frequencies

The harmonic vibrational frequencies for the five equilibrium structures, as well as the total energies, and dipole moments, are presented in Tables 1–5.

5.2.1. $\tilde{X}^1\Sigma_g^+$ *ground state.* The average absolute percentage differences between the predicted and experimental [60] harmonic vibrational frequencies are 11.5, 11.9, 12.3, 13.2, and 13.1% at the SCF level of theory with the five increasingly large basis sets. The corresponding values at the CISD level of theory with the DZP, TZ2P, and QZ3P basis sets are 2.2, 2.4, and 2.8%, respectively. At the QZ(3df, 3pd)-SCF level of theory the largest deviations between *ab initio* theoretical and experimental values are observed for the two bending modes, 30.3%(π_g) and 16.2%(π_u), probably due in part to underestimation of the C–C and C–H bond lengths. At the QZ3P-CISD level of theory the largest error of 5.0% is again attributed to the π_g bending mode. The improvement in predicting the harmonic vibrational frequencies at the CISD level relative to the SCF level is very substantial. Considering the accuracy of predictions for the acetylene ground state it is reasonable to expect similar accuracy (with perhaps slightly larger error bars) for the harmonic vibrational frequencies of the triplet states.

5.2.2. Triplet states. The C–H and C–C stretching vibrational frequencies of the triplet states are all red-shifted relative to the corresponding vibrational modes of the ground state. For the $^3B_2$ state, the symmetric and asymmetric C–H stretching modes are red-shifted 363 and 288 cm^{-1} at the QZ(3df, 3pd)-SCF level and 377 and 312 cm^{-1} at the QZ3P-CISD level of theory. The C–C stretching frequency is lowered 462 cm^{-1} at the QZ(3df, 3pd)-SCF level and 437 cm^{-1} at the QZ3P-CISD level of theory. The longer C–H and C–C bond lengths of the triplet state relative to those of the ground state are apparently responsible for these red-shifts. The C–C stretching (harmonic) frequency for the C_2H_4 molecule is experimentally determined to be 1655 cm^{-1} [63]. Thus the experimental difference in the C–C stretching frequencies for the ground state

Table 1. Theoretical predictions of the physical properties for the C_2H_2 ground state ($\tilde{X}\,^1\Sigma_g^+$)[a,b]

Level of theory	Energy	ω_1 σ_g^+	ω_2 σ_g^+	ω_3 σ_u^+	ω_4 π_g	ω_5 π_u	ZPVE
DZP-SCF	−76.831 903	3677	2203	3571	767	858	18.16
TZ2P-SCF	−76.849 388	3671	2208	3556	785	855	18.18
QZ3P-SCF	−76.852 231	3660	2210	3549	798	858	18.20
TZ(2df, 2pd)-SCF	−76.852 641	3668	2210	3556	813	870	18.30
QZ(3df, 3pd)-SCF	−76.855 059	3666	2211	3555	813	868	18.29
DZP-CISD	−77.082 305	3573	2072	3478	611	760	16.96
TZ2P-CISD	−77.124 287	3572	2089	3459	613	766	16.98
QZ3P-CISD	−77.132 427	3556	2087	3455	593	763	16.88
TZ(2df, 2pd)-CISD	−77.150 441	—	—	—	—	—	—
QZ(3df, 3pd)-CISD	−77.155 965	—	—	—	—	—	—
DZP-CISDT	−77.091 452	—	—	—	—	—	—
TZ2P-CISDT[c]	−77.136 352	—	—	—	—	—	—
expt.[d]		3495	2008	3415	624	747	—

[a] Energies are in hartree, harmonic vibrational frequencies in cm^{-1} and zero point vibrational energies (ZPVE) in kcal · mol^{-1}

[b] With inclusion of the Davidson correction, the CISD + Q energies are −77.106 187, −77.150 961, −77.159 778, −77.179 436 and −77.185 374 hartree for the DZP, TZ2P, QZ3P, TZ(2df, 2pd) and QZ(3df, 3pd) basis sets, respectively

[c] Energy at the CISD optimized geometry is −77.136 322 hartree

[d] Harmonic vibrational frequencies are from [60]

Table 2. Theoretical predictions of the physical properties for *cis*-C_2H_2 ($\tilde{a}\,^3B_2$),[a,b] the lowest triplet state of acetylene

Level of theory	Energy	μ	ω_1 a_1	ω_2 a_1	ω_3 a_1	ω_4 a_2	ω_5 b_2	ω_6 b_2	ZPVE
DZP-SCF	−76.731 917	1.277	3336	1752	909	936	3302	1213	16.37
TZ2P-SCF	−76.744 950	1.167	3316	1748	913	947	3278	1216	16.32
QZ3P-SCF	−76.747 773	1.148	3300	1747	911	945	3264	1216	16.27
TZ(2df, 2pd)-SCF	−76.747 342	1.177	3304	1749	911	955	3267	1213	16.30
QZ(3df, 3pd)-SCF	−76.750 012	1.146	3303	1749	911	954	3267	1215	16.30
DZP-CISD	−76.956 872	1.274	3219	1646	856	793	3186	1147	15.51
TZ2P-CISD	−76.991 638	1.178	3195	1642	857	808	3155	1133	15.43
QZ3P-CISD	−77.000 816	1.159	3179	1650	854	814	3143	1138	15.41
TZ(2df, 2pd)-CISD	−77.015 500	1.196	—	—	—	—	—	—	—
QZ(3df, 3pd)-CISD	−77.022 098	1.168	—	—	—	—	—	—	—
DZP-CISDT	−76.966 870	1.279	—	—	—	—	—	—	—
TZ2P-CISDT[c]	−77.004 642	—	—	—	—	—	—	—	—

[a] Energies are in hartree, dipole moments (μ) in debye, harmonic vibrational frequencies in cm^{-1} and zero point vibrational energies (ZPVE) in kcal · mol^{-1}

[b] With inclusion of the Davidson correction, the CISD + Q energies are −76.978 382, −77.015 494, −77.025 413, −77.041 240 and −77.048 305 hartree for the DZP, TZ2P, QZ3P, TZ(2df, 2pd) and QZ(3df, 3pd) basis sets, respectively

[c] At the CISD optimized geometry

Table 3. Theoretical predictions of the physical properties for *trans*-C_2H_2 ($\tilde{b}\ ^3B_u$)^{a,b}

Level of theory	Energy	ω_1 a_g	ω_2 a_g	ω_3 a_g	ω_4 a_u	ω_5 b_u	ω_6 b_u	ZPVE
DZP-SCF	−76.720 007	3374	1737	1205	1008	3358	863	16.51
TZ2P-SCF	−76.733 300	3357	1735	1209	1012	3341	869	16.47
QZ3P-SCF	−76.736 091	3340	1734	1207	1011	3324	868	16.42
TZ(2df, 2pd)-SCF	−76.735 559	3346	1735	1205	1016	3329	865	16.44
QZ(3df, 3pd)-SCF	−76.738 248	3344	1736	1206	1015	3328	866	16.43
DZP-CISD	−76.943 802	3285	1624	1145	924	3268	808	15.80
TZ2P-CISD	−76.979 104	3268	1624	1135	931	3252	806	15.75
QZ3P-CISD	−76.988 105	3246	1631	1134	925	3228	803	15.68
TZ(2df, 2pd)-CISD	−77.002 481	—	—	—	—	—	—	—
QZ(3df, 3pd)-CISD	−77.009 126	—	—	—	—	—	—	—
DZP-CISDT	−76.953 757	—	—	—	—	—	—	—
TZ2P-CISDT[c]	−76.991 926	—	—	—	—	—	—	—

[a] Energies are in hartree, harmonic vibrational frequencies in cm^{-1} and zero point vibrational energies (ZPVE) in kcal · mol^{-1}

[b] With inclusion of the Davidson correction, the CISD + Q energies are −76.965 512, −77.002 991, −77.012 697, −77.028 127 and −77.035 238 hartree for the DZP, TZ2P, QZ3P, TZ(2df, 2pd) and QZ(3df, 3pd) basis sets, respectively

[c] At the CISD optimized geometry

Table 4. Theoretical predictions of the physical properties for *trans*-C_2H_2 ($\tilde{c}\ ^3A_u$)^{a,b,c}

Level of theory	Energy	ω_1 a_g	ω_2 a_g	ω_3 a_g	ω_4 a_u	ω_5 b_u	ω_6 b_u
DZP-SCF	−76.699 056	3293	1534	1188	(956)	(3284)	(1709)
TZ2P-SCF	−76.712 139	3272	1533	1187	(967)	(3265)	(1994)
QZ3P-SCF	−76.715 331	3258	1536	1187	(967)	(3250)	(1906)
TZ(2df, 2pd)-SCF	−76.713 877	3262	1537	1178	(965)	(3254)	(2019)
QZ(3df, 3pd)-SCF	−76.716 849	3262	1539	1178	(967)	(3254)	(1942)
DZP-CISD	−76.931 196	3182	1434	1169	—	—	—
TZ2P-CISD	−76.966 335	3165	1434	1149	—	—	—
QZ3P-CISD	−76.976 222	3145	1448	1159	—	—	—
TZ(2df, 2pd)-CISD	−76.989 933	—	—	—	—	—	—
QZ(3df, 3pd)-CISD	−76.997 276	—	—	—	—	—	—
DZP-CISDT	−76.943 770	—	—	—	—	—	—
TZ2P-CISDT[d]	−76.982 630	—	—	—	—	—	—

[a] Energies are in hartree, harmonic vibrational frequencies in cm^{-1} and zero point vibrational energies (ZPVE) in kcal · mol^{-1}

[b] With inclusion of the Davidson correction, the CISD + Q energies are −76.953 264, −76.991 076, −77.001 829, −77.016 757 and −77.024 679 hartree for the DZP, TZ2P, QZ3P, TZ(2df, 2pd) and QZ(3df, 3pd) basis sets, respectively

[c] Vibrational frequencies in parentheses are for non-totally symmetric modes. They may not be entirely reliable (see text)

[d] At the CISD optimized geometry

Table 5. Theoretical predictions of the physical properties for *cis*-C_2H_2 ($\tilde{d}\,^3A_2$)^{a,b,c}

Level of theory	Energy	μ	ω_1 a_1	ω_2 a_1	ω_3 a_1	ω_4 a_2	ω_5 b_2	ω_6 b_2
DZP-SCF	−76.678 028	2.413	3288	1669	889	(1104)	(3277)	(1897)
TZ2P-SCF	−76.701 421	2.279	3264	1669	885	(1115)	(3264)	(2111)
QZ3P-SCF	−76.704 270	2.241	3247	1667	882	(1113)	(3241)	(2013)
TZ(2df, 2pd)-SCF	−76.703 257	2.267	3254	1670	881	(1114)	(3263)	(2125)
QZ(3df, 3pd)-SCF	−76.706 078	2.226	3252	1670	881	(1113)	(3253)	(2046)
DZP-CISD	−76.917 539	2.285	3165	1552	853	(1048)	—	—
TZ2P-CISD	−76.954 843	2.165	3140	1555	855	(1049)	—	—
QZ3P-CISD	−76.964 331	2.130	3124	1561	850	(1052)	—	—
TZ(2df, 2pd)-CISD	−76.978 785	2.158	—	—	—	—	—	—
QZ(3df, 3pd)-CISD	−76.985 794	2.125	—	—	—	—	—	—
DZP-CISDT	−76.929 891	2.251	—	—	—	—	—	—
TZ2P-CISDT^d	−76.970 265	—	—	—	—	—	—	—

[a] Energies are in hartree, dipole moments (μ) in debye, harmonic vibrational frequencies in cm^{-1} and zero point vibrational energies (ZPVE) in kcal · mol^{-1}

[b] With inclusion of the Davidson correction, the CISD + Q energies are −76.939 139, −76.979 238, −76.989 579, −77.005 255 and −77.012 838 hartree for the DZP, TZ2P, QZ3P, TZ(2df, 2pd) and QZ(3df, 3pd) basis sets, respectively

[c] Vibrational frequencies in parentheses are for non-totally symmetric modes. They may not be entirely reliable (see text)

[d] At the CISD optimized geometry

C_2H_2 and C_2H_4 molecules is 353 (2008−1655) cm^{-1}, reflecting the increase in the C–C bond length of 0.127 (1.330 − 1.203) Å. It is interesting to note that the predicted red-shift of 437 cm^{-1} for the $^3B_2$ state at the QZ3P-CISD level of theory is larger than that of the value of 353 cm^{-1} shown above.

The ground state of acetylene has two degenerate bending modes, $\omega_4(\pi_g)$ and $\omega_5(\pi_u)$. The sum of these four bending frequencies $(2\omega_4 + 2\omega_5)$ is 3362 cm^{-1} at the QZ(3df, 3pd)-SCF level and 2712 cm^{-1} at the QZ3P-CISD levels of theory, respectively. For the $^3B_2$ state, the sum of the bending frequencies $(\omega_3 + \omega_4 + \omega_6)$ is 3080 cm^{-1} at the QZ(3df, 3pd)-SCF level and 2806 cm^{-1} at the QZ3P-CISD level of theory. The difference in the sums of bending frequencies for the $^1\Sigma_g^+$ and $^3B_2$ states is 282 cm^{-1} (increase) at the SCF level and 94 cm^{-1} (decrease) at the CISD level of theory. It can be seen by comparison that the structural change upon an electronic excitation according to Eq. (2) reflects a substantial lowering of the C–H and C–C stretching frequencies and only a marginal lowering of bending frequencies.

For the ^3B_u state, the symmetric and asymmetric C–H stretching modes are red-shifted by 322 and 227 cm^{-1} at the QZ(3df, 3pd)-SCF level and by 310 and 227 cm^{-1} at the QZ3P-CISD level of theory. Relative to the $^3B_2$ state the slightly smaller red-shifts of the C–H stretches may be attributed to the shorter C–H bond length of the ^3B_u state. The C–C stretching frequency decreases by 475 cm^{-1} at the QZ(3df, 3pd)-SCF level and 456 cm^{-1} at the QZ3P-CISD level of theory. As was the case in the $^3B_2$ state, this difference is again larger than the ground state acetylene-ground state ethylene value of 353 cm^{-1}. The difference in the sums of bending frequencies for the $^1\Sigma_g^+$ and ^3B_u states is 275 cm^{-1} (increase) at the QZ(3df, 3pd)-SCF level and 150 cm^{-1} (decrease) at the QZ3P-CISD level of theory. Thus the structural change upon an electronic excitation in configuration (2) again is associated with the significant lowering of the C–H and C–C stretching frequencies.

As already mentioned in the section designated "Stability of the SCF wavefunctions," the non-totally symmetric vibrations for the ^3A_u and $^3A_2$ states may not be reliable, especially for the a_u and b_u modes of the former state and the b_1 and b_2 modes of the latter state owing to the instability MO rotations. In Tables 4 and 5 non-totally symmetric vibrational frequencies are shown in parentheses at the SCF level and only totally symmetric frequencies and the a_2 frequency for the $^3A_2$ state are obtained at the CISD level of theory. For these ^3A states the SCF asymmetric C–H stretching (b_u and b_2) and torsional (a_u and a_2) modes appear to have reasonable magnitudes. However, the asymmetric C–H bending (b_u and b_2) modes display unphysically large values. Such anomalous behavior can be attributed to the instability of the SCF wavefunctions for the ^3A_u and $^3A_2$ states [38]

Wendt, Hippler, and Hunziker were able to detect three vibrational features for the $^3A_2$ state [30]. They assigned the experimental (fundamental) frequency of 1466 cm^{-1} to the C–C stretching mode which agrees well with the *ab initio* harmonic values of 1581 cm^{-1} by Lischka and Karpfen [31] and 1561 cm^{-1} in the present research, when a typical scaling factor from harmonic to anharmonic frequency of 0.92–0.96 at the CISD level [64–66] is taken into account. In the case of the C_2D_2 molecule our theoretical harmonic vibrational frequency for the C–C stretching mode is 1512 cm^{-1}. Thus, the isotopic shift for this C–C stretching frequency is here predicted to be 49 (1561 – 1512) cm^{-1}, which is in good agreement with the experimentally estimated value of 53 (1466 – 1413) cm^{-1}. On the other hand, the experimentalists were unable to assign their other two observed vibrational frequencies at 1043 and 771 cm^{-1} for C_2H_2 and at 828 and 558 cm^{-1} for C_2D_2. Predicted harmonic vibrational frequencies of 878 cm^{-1} from Lischka's study [31] and 850 cm^{-1} from our work clearly suggest that the absorption at 771 cm^{-1} is the symmetric CCH bending. For the deuterated molecule the corresponding frequency is predicted to be 611 cm^{-1} at the QZ3P-CISD level of theory. The predicted isotopic shift for this mode is 239 (850 – 611) cm^{-1}. This shift agrees quite well with the experimental value of 213 (771 – 558) cm^{-1}. Finally the experimental fundamental at 1043 cm^{-1} may be assigned to the torsional mode by comparing with the SCF values (with different basis sets) of about 1100 cm^{-1} and CISD values near 1050 cm^{-1}. Although these SCF wavefunctions suffer from instability, the a_2 MO rotations related to the torsional mode are *not* involved in the instability [38]. Thus the $^3A_2$ state SCF frequency at about 1100 cm^{-1} and CISD frequency at about 1050 cm^{-1} may be reliable, and appear to fall in a reasonable range as a torsional mode for molecules with C–C double bonds. The *ab initio* harmonic frequency for the torsional mode of the $^3A_2$ state C_2D_2 molecule is 835 cm^{-1}. The predicted isotopic shift of 217 (1052 – 835) cm^{-1} is again consistent with the experimental value of 215 (1043 – 828) cm^{-1}.

5.3. *Dipole moments*

With the largest basis set, QZ(3df, 3pd), the dipole moments for the $^3B_2$ and $^3A_2$ states are 1.15 and 2.23 debye at the SCF level and 1.17 and 2.13 debye at the CISD level of theory, respectively. At both levels of theory the predicted dipole moments decrease more than 0.1 debye when the second set of polarization functions are added to the basis set. The effect of the third set of *d* functions and the set of *f* functions appears to be much less than that of the second set of polarization functions. Since the excitation given in Eq. (8) removes an electron from an orbital perpendicular to the C_2 axis and places it in an orbital parallel to the C_2 axis, the dipole moment is significantly larger in the $^3A_2$ state compared to the $^3B_2$ state.

5.4. *Energetics*

The CCSD and CCSD(T) energies determined at the CISD optimized geometries are shown in Table 6. Using the energetic information presented in Tables 1through 6, relative energies between the ground and triplet states are obtained and the results are summarized in Table 7. In this table the values in parentheses are those corrected with the zero point vibrational energies (ZPVE). For the CISD + Q, CISDT, CCSD and CCSD(T) wavefunctions, the CISD ZPVE values for the corresponding basis set were employed. Compared to more reliable CISD and CCSD methods the SCF wavefunctions significantly underestimate the energy separation between the ground and triplet states. At the SCF level a triplet state is usually preferentially stabilized relative to a closed shell due to the fact that the open-shell electrons may avoid each other rather effectively. Therefore the inclusion of electron correlation favorably stabilizes the closed-shell ground state with respect to the excited triplet states.

At the SCF level the relative energies of all the triplet states increase with expansion of the basis set size by about 2 to 3 kcal/mol relative to the values with the DZ + P basis set. This energy separation due to the basis set enhancement is even more prominent at the CISD and CISD + Q levels of theory. By adding the second and third sets of polarization functions relative energies increase about 3 to 4 kcal/mol with respect to the values with the DZ + P basis set for all the triplet states. Inclusion of the *d* (for H) and *f* (for C) functions further increase the energy separation about 1.5 to 2 kcal/mol.

The CISDT wavefunctions with the DZP and TZ2P basis sets represent very similar energy gaps between the ground and excited triplet states as those from the CISD level. The effects of triple excitations are known to be much smaller than those due to quadruple excitations (see for example [67]).

Relative energies determined by the CCSD method show very close agreement with the results from the CISD + Q method. As a matter of fact, for all cases the predicted relative energies via two methods are consistent within 0.5 kcal/mol of deviation. Thus it is evident that for the C_2H_2 system the CISD + Q and CCSD levels of theory provide very similar descriptions of effects of electronic correlation on the relative energies at the CISD optimized geometries.

At the CCSD(T) level of theory relative energies further increase by about 1.5 to 2 kcal/mol with respect to those predicted at the CCSD level. With the

Table 6. The CCSD and CCSD(T) energies (in hartrees) for the ground state and the four lowest triplet states of C_2H_2[a]

Level of theory	$\tilde{X}^1\Sigma_g^+$	$\tilde{a}\,^3B_2$	$\tilde{b}\,^3B_u$	$\tilde{c}\,^3A_u$	$\tilde{d}\,^3A_2$
DZP-CCSD	−77.102 477	−76.973 945	−76.961 238	−76.948 844	−76.934 949
TZ2P-CCSD	−77.146 260	−77.010 521	−76.998 159	−76.986 189	−76.974 562
QZ3P-CCSD	−77.154 945	−77.020 336	−77.007 772	−76.996 834	−76.984 801
TZ(2df, 2pd)-CCSD	−77.174 270	−77.036 003	−77.023 039	−77.011 584	−77.000 282
QZ(3df, 3pd)-CCSD	−77.180 116	−77.043 007	−77.030 095	−77.019 436	−77.007 800
DZP-CCSD(T)	−77.113 282	−76.982 825	−76.970 589	−76.958 043	−76.943 939
TZ2P-CCSD(T)	−77.160 930	−77.022 306	−77.010 207	−76.998 419	−76.986 601
QZ3P-CCSD(T)	−77.170 411	−77.032 847	−77.020 515	−77.009 825	−76.997 629
TZ(2df, 2pd)-CCSD(T)	−77.190 560	−77.049 161	−77.036 362	−77.025 326	−77.013 831
QZ(3df, 3pd)-CCSD(T)	−77.196 919	−77.056 627	−77.043 862	−77.033 682	−77.021 871

[a] Energies were evaluated at the CISD optimized geometries with the corresponding basis set

largest basis set, QZ(3df, 3pd), the classical energy separations T_e of the four triplet states relative to the ground state are 88.0, 96.0, 102.4, and 109.8 kcal/mol, respectively. The increases in energy separation for the four triplet states with this QZ(3df, 3pd)-CCSD(T) method compared to the DZP-SCF method are 25.3 (88.0 − 62.7), 25.8 (96.0 − 70.2), 19.0 (102.4 − 83.4), and 18.9 (109.8 − 90.9) kcal/mol, respectively. Taking the $^3B_2$ state as an example, the increase of 25.3 kcal/mol in T_e may be approximately separated into three contributions; 1) correlation effects of 19.2 (81.9 − 62.7) kcal/mol, 2) polarization effects of 4.4 (86.3 − 81.9) kcal/mol, and 3) higher angular momentum polarization function effects of 1.7 (88.0 − 86.3) kcal/mol. It is important to realize that inclusion of higher order excitations (more than singles and doubles) in the correlated wavefunction *and* use of the basis set with multiple polarization functions and higher angular momentum polarization function(s) are necessary in order to obtain theoretical results reliable to within 2 kcal/mol.

For the two lowest triplet states the relative QZ(3df, 3pd)-CCSD(T) energies but including the ZPVE corrections at the QZ3P-CISD level are 86.6 (3.75; 30,270) and 94.8 (4.11; 33,170) kcal/mol with results in parentheses given in units of (eV; cm^{-1}), respectively. The energy separation of the $^3B_2$ and ^3B_u states is predicted to be 8.2 (0.36) kcal/mol(eV) which is in close agreement with out previous value of 8.0 (0.35) kcal/mol(eV) [29]. However, note that the latter value did not include the ZPVE correction [29].

The energy difference for the $^3B_2$–$^3A_2$ electronic transition given in Eq. (8) is experimentally determined to be 7388 cm^{-1} [30]. The theoretical values without the ZPVE correction are 9640, 7970, 7780, 7730, and 7630 cm^{-1} at the SCF, CISD, CISD + Q, CCSD and CCSD(T) levels of theory with the QZ(3df, 3pd) basis set and 7540 cm^{-1} using the TZ2P-CISDT method. Although the harmonic vibrational frequencies of the non-totally symmetric modes are not available for the $^3A_2$ state, the ZVPE correction from the totally symmetric and a_2 modes of +45 cm^{-1} at the QZ3P-CISD level may be a good estimate. Thus our predicted value for the energy separation between the $^3B_2$ and $^3A_2$ states is 7680 (7630 + 50) cm^{-1} at the QZ(3df, 3pd)-CCSD(T) level of theory, which is

Table 7. Relative energies (kcal · mol^{-1}) for the four lowest triplet states of C_2H_2[a]

Level of theory	$\tilde{X}^1\Sigma_g^+$	$\tilde{a}\,^3B_2$	$\tilde{b}\,^3B_u$	$\tilde{c}\,^3A_u$	$\tilde{d}\,^3A_2$
DZP-SCF	0.0	62.74 (60.95)	70.22 (68.57)	83.36	90.91
TZ2P-SCF	0.0	65.54 (63.68)	72.85 (71.14)	86.12	92.85
OZ3P-SCF	0.0	65.55 (63.62)	72.88 (71.10)	85.91	92.85
TZ(2df, 2pd)-SCF	0.0	66.08 (64.08)	73.47 (71.61)	87.07	93.74
QZ(3df, 3pd)-SCF	0.0	65.92 (63.93)	73.30 (71.44)	86.73	93.49
DZP-CISD	0.0	78.71 (77.26)	86.91 (85.75)	94.82	103.39
TZ2P-CISD	0.0	83.24 (81.69)	91.10 (89.87)	99.12	106.33
OZ3P-CISD	0.0	82.59 (81.12)	90.56 (89.36)	98.02	105.48
TZ(2df, 2pd)-CISD	0.0	84.68 (—)	92.85 (—)	100.72	107.71
QZ(3df, 3pd)-CISD	0.0	84.00 (—)	92.14 (—)	99.58	106.78
DZP-CISD + Q[b]	0.0	80.20 (78.75)	88.27 (87.11)	95.96	104.82
TZ2P-CISD + Q[b]	0.0	85.01 (83.46)	92.85 (91.62)	100.33	107.76
QZ3P-CISD + Q[b]	0.0	84.31 (82.84)	92.29 (91.09)	99.11	106.80
TZ(2df, 2pd)-CISD + Q[b]	0.0	86.72 (—)	94.95 (—)	102.08	109.30
QZ(3df, 3pd)-CISD + Q[b]	0.0	86.01 (—)	94.20 (—)	100.82	108.27
DZP-CISDT	0.0	78.18 (76.73)	86.40 (85.24)	92.67	101.38
TZ2P-CISDT[b]	0.0	82.63 (81.08)	90.61 (89.38)	96.44	104.20
DZP-CCSD[b]	0.0	80.65 (79.20)	88.63 (87.47)	96.41	105.12
TZ2P-CCSD[b]	0.0	85.18 (83.63)	92.93 (91.70)	100.45	107.74
QZ3P-CCSD[b]	0.0	84.47 (83.00)	92.35 (91.15)	99.22	106.77
TZ(2df, 2pd)-CCSD[b]	0.0	86.76 (—)	94.90 (—)	102.09	109.18
QZ(3df, 3pd)-CCSD[b]	0.0	86.04 (—)	94.14 (—)	100.83	108.13
DZP-CCSD(T)[b]	0.0	81.86 (80.41)	89.54 (88.38)	97.41	106.26
TZ2P-CCSD(T)[b]	0.0	86.99 (85.44)	94.58 (93.35)	101.98	109.39
QZ3P-CCSD(T)[b]	0.0	86.32 (84.85)	94.06 (92.86)	100.77	108.42
TZ(2df, 2pd)-CCSD(T)[b]	0.0	88.73 (—)	96.76 (—)	103.68	110.90
QZ(3df, 3pd)-CCSD(T)[b]	0.0	88.03 (—)	96.04 (—)	102.43	109.84

[a] ΔE values are based on the total energies in Tables 1–6. The values in parentheses are those including the ZPVE correction at the same level of theory

[b] Energies were evaluated at the CISD optimized geometries using CISD ZPVE corrections from the same basis set

in excellent agreement with the experimental observation of 7388 cm^{-1} [30]. In practice the correlated wavefunctions including higher than single and double excitations predict the energy separation of these two triplet states quite satisfactorily.

6. Conclusions

Four low-lying triplet electronic states as well as the ground state of the acetylene molecule have been investigated at rather high levels of theory. Complete geometry optimizations and vibrational analyses were performed at the SCF and CISD levels of theory with large basis sets. Structures were also determined at the CISDT level, including all triple excitations.

The SCF wavefunctions of the lower two states, ${}^3B_2$ and ${}^3B_u$, were found to be stable, while those of the two upper states, ${}^3A_u$ and ${}^3A_2$, were determined to be unstable. Although the physical properties of the ${}^3B$ states are believed to be reliable, those of the ${}^3A$ states, especially non-totally symmetric properties are considered to be less reliable.

The correlation effects are included using the CISD, CISD + Q, CISDT, CCSD, and CCSD(T) methods. The earlier predicted energy ordering [29] of ${}^3B_2 < {}^3B_u < {}^3A_u < {}^3A_2$ is confirmed in the current high level study. However, the excitation energies of the triplet states increase with expansion of the basis set and increasing excitation levels in the configuration interaction space, up to 7.5 kcal/mol compared to previous theoretical research [29].

It is demonstrated that the inclusion of higher excitations (higher than singles and doubles) and use of basis sets with multiple polarization functions as well as higher angular momentum polarization function(s) is necessary in order to obtain predictions reliable to within an accuracy of 2.0 kcal/mol. We hope that these definitive theoretical predictions will provide a stimulus for the full experimental characterization of the lowest triplet states of acetylene, including the identification for the first time of the two lowest *trans* states.

Acknowledgements. We thank Professor R. W. Field and Dr. J. K. Lundberg at Massachusetts Institute of Technology for their informative suggestions and for encouragement in initiating this study. We are very grateful to Dr. Roger S. Grev for many stimulating and informative discussions. This research was supported by the U.S. Department of Energy.

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