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The Equilibrium Geometry, Harmonic Vibrational Frequencies, and Estimated ab Initio Limit for the Barrier to Planarity of the Ethylene Radical Cation

Micah L. Abrams, Edward F. Valeev, and C. David Sherrill*

Center for Computational Molecular Science and Technology, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

T. Daniel Crawford

Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24060

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The equilibrium geometry, barrier to planarity, and harmonic vibrational frequencies were determined theoretically for the ground state of the ethylene radical cation using several quantum mechanical methods and basis sets. The minimum-energy structure is a nonplanar D_2 conformer separated from its symmetry equivalent by a planar transition state. The CCSD(T)/cc-pVTZ level of theory obtained an equilibrium C−C bond length and torsion angle of 1.4004 Å and 21.0°, respectively, which are 0.005 Å and 4.0° less than the experimentally derived values of Köppel et al. [*J. Chem. Phys*. **1978**, *69*, 4252]. The documented reliability of CCSD(T)/cc-pVTZ equilibrium geometries might call into question the experimentally derived geometry. In addition, the barrier to planarity was determined using a series of basis sets and methods aimed at reaching the complete-basis-set limit. The final vibrationless barrier was determined to be 116 ± 35 cm^{-1}. Also, to aid in the interpretation of a recent infrared cavity-ring-down experiment, the harmonic vibrational frequencies were determined at the CCSD(T)/TZ2P level of theory. After the harmonic frequencies were scaled by a factor to account for incompleteness in the basis set and electron correlation treatment, the difference between the theoretically and experimentally deduced $\omega_7(b_1)$ frequencies was a mere 1.4%.

1. Introduction

The values for the torsion angle and barrier to planarity of the ethylene radical cation have been the topic of controversy for nearly 20 years. This is surprising considering that this molecule is the simplest possible unsaturated hydrocarbon radical cation. The controversy began in 1978 when Köppel and co-workers[1] computed the vibrational structure of the first band ($^2B_{3u}$) in the photoelectron spectrum (PES) of neutral ethylene. The Hartree−Fock and many-body methods utilized in the study took into account the vibronic coupling of the $^2B_{3u}$ ground state and $^2B_{3g}$ first excited state of the ion, both with D_{2h} symmetry. After adjusting the energy separation between the $^2B_{3u}$ and $^2B_{3g}$ states, the frequency of the ω_4 vibrational mode, and the vibronic coupling constant to fit the PES of neutral ethylene, they concluded that the ground state was nonplanar with a torsion angle and barrier to planarity of approximately 25° and 234 cm^{-1}, respectively.

Prior to the study by Köppel and co-workers, there had been no definitive prediction of the torsion angle of the cation. Semiempirical studies[2,3] predicted a twisted D_2 structure but disagreed with Hartree−Fock studies[4−7] that predicted a planar D_{2h} structure. However, in 1984, Handy and co-workers[8] found a torsion angle of 20.1° using second-order Møller−Plesset perturbation theory (MP2) and a small 3-21G basis. They also estimated the barrier to planarity to be ∼100 cm^{-1} using the CEPA-1 (coupled electron pair approximation) and a series of Pople basis sets from 3-21G to 6-311G(df,p). More recently, Salhi-Benachenhou et al.,[9] using the quadratic configuration interaction method with single, double, and perturbative triple excitations [QCISD(T)] and a 6-311G(d,p) basis set, found a torsion angle of 20.2°. At that geometry, coupled-cluster calculations with single, double, and perturbative triple excitations [CCSD(T)] and QCISD(T) with a 6-311++G(2df,p) basis set found the barrier to planarity to be 87 and 104 cm^{-1}, respectively.

Density functional methods have also been used to address the ethylene radical cation structural dilemma. Errikson et al.,[10] using the gradient-corrected Becke exchange and Perdew correlation functional (BP) and a DZP basis, found a torsion angle of 33°, whereas Liu et al.,[11] using B3LYP [the Becke three-parameter hybrid exchange functional (B3) with the correlation functional of Lee−Yang−Parr (LYP)] and a 6-311G(d,p) basis, found a torsion angle of 28.4°.

On the experimental front, more recent studies by Toriyama and Okazaki[12,13] utilized ESR techniques to analyze the hyperfine couplings of ^1H and ^{13}C. They estimated the torsion angle of the cation to be between 8° and 23°. Therefore, the most recent theoretical and experimental data suggest a twisted D_2 structure for the ethylene radical cation with a torsion angle and barrier to planarity as small as 8° and 80 cm^{-1} or as large as 35° and 250 cm^{-1}, respectively.

Several research groups have also analyzed the vibrational spectrum of the cation. From the photoelectron spectrum of neutral ethylene, Pollard et al.[14] assigned the $\omega_2(a_g)$ C−C stretching mode and the $\omega_3(a_g)$ H−C−H bending mode of the cation. Somasundram and Handy[15] used scaled Hartree−Fock calculations of neutral ethylene to verify the results of Pollard

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* Author to whom correspondence should be addressed. E-mail: sherrill@chemistry.gatech.edu.

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et al., but only for two of the possible 12 modes. Recently, Draves and Taylor,[16] utilizing infrared cavity-ring-down spectroscopy, observed and assigned the $\omega_7(b_1)$ CH_2 wagging mode.

The goals of the present study are three-fold: (1) to determine the equilibrium geometry of the cation using state of the art ab initio techniques; (2) to obtain a definitive estimate for the barrier to planarity using the basis-set-limit extrapolation techniques suggested by Feller[17] and Helgaker, Klopper, Koch, and Noga;[18] and (3) to obtain harmonic vibrational frequencies for comparison with experimental assignments.

2. Methods Section

We determined the equilibrium geometry, barrier to planarity, and harmonic vibrational frequencies of the $^2B_3$ ground state[19] of the ethylene radical cation using several theoretical methods and basis sets.

Geometry optimizations were performed using all-electron B3LYP,[20] MP2,[21] CCSD,[22] and CCSD(T)[23] methods with spin-unresticted orbitals. Energy gradients were evaluated analytically in all cases.[24] The four methods employed three different Gaussian basis sets: DZP,[25] TZ2P,[26] and cc-pVTZ.[27] The DZP basis is the standard double-ζ set of Huzinaga and Dunning augmented with a set of d functions on carbon and a set of p functions on hydrogen, denoted C(9s5p1d/4s2p1d) and H(4s1p/2s1p), respectively. The TZ2P basis is the standard triple-ζ set of Dunning augmented with two sets of d functions on carbon and two sets of p functions on hydrogen, denoted C(10s6p2d/5s3p2d) and H(5s2p/3s2p), respectively. The largest basis used in optimizing the geometry is the correlation-consistent polarized-valence triple-ζ set of Dunning and co-workers with the C(10s5p2d1f/4s3p2d1f) and H(5s2p1d/3s2p1d) contraction scheme. Spherical harmonics were employed for all Dunning correlation-consistent basis sets.

The barrier to planarity was determined by subtracting the energy of the fully optimized structure of D_2 symmetry from the energy of the planar transition state. The Hartree−Fock contribution to the barrier was determined using Dunning's cc-pVXZ ($X = 3, 4, 5$) and aug-cc-pVXZ ($X = 3, 4, 5$) basis sets, where aug- specifies the cc-pVXZ basis augmented by a single diffuse function per angular momentum (1s1p1d1f for $X = 3$, 1s1p1d1f1g for $X = 4$, and 1s1p1d1f1g1h for $X = 5$).[28] The valence MP2 and valence CCSD(T) contributions to the barrier were determined using Dunning's cc-pVXZ ($X = 3, 4$) and aug-cc-pVXZ ($X = 3, 4$) basis sets. The valence CCSD with complete treatment of triple excitations (CCSDT)[29] contribution to the barrier was determined using Dunning's cc-pVXZ ($X = 2, 3$) basis sets. To isolate the contribution of the quadruple excitations to the barrier, labeled [Q], the total energy of the Brueckner-reference[30] coupled-cluster method with double excitations and perturbative triples, B-CCD(T), was subtracted from the total energy of B-CCD(TQ)[31] at both the twisted minimum and planar transition states. Because of the expense of the B-CCD(TQ) calculations, we were restricted to the small cc-pVDZ basis set.

For the valence contribution to the barrier, the 1s core orbitals of the carbon atoms were constrained to be doubly occupied. Core correlation effects were then determined at the MP2 level of theory from all-electron treatments with Dunning's cc-pCVXZ ($X = 3, 4$) basis sets.[32] Relativistic effects were considered by a perturbative treatment of the Cowan−Griffin quasirelativistic many-electron Hamiltonian, which includes the mass-velocity and one-electron Darwin operators, using the CCSD(T) relaxed density and the cc-pCVTZ basis.[33]

Harmonic vibrational frequencies were determined using analytic second derivatives[34] for the B3LYP/cc-pVTZ and CCSD(T)/(DZP, TZ2P, cc-pVTZ) levels of theory. The Hartree−Fock calculations were performed with PSI 3.0;[35] MP2 and B3LYP calculations were performed with Q-Chem 2.0;[36] CCSD, CCSD(T), and CCSDT calculations were performed with ACESII;[37] and B-CCD(T) and B-CCD(TQ) calculations were performed with Gaussian 98.[38]

TABLE 1: Geometry and Barrier to Planarity of the Ethylene Radical Cation[a,b]

method/basis	r_{CC}	r_{CH}	θ_{HCC}	τ	ΔE_e
MP2/DZP	1.4271	1.0906	120.4	0.0	0.0
	1.4271	1.0906	120.4	0.0	
MP2/TZ2P	1.4099	1.0804	120.5	10.3	3.7
	1.4127	1.0800	120.5	0.0	
MP2/cc-pVTZ	1.4049	1.0785	120.5	12.5	7.7
	1.4090	1.0780	120.4	0.0	
CCSD/DZP	1.4256	1.0933	120.5	11.0	5.9
	1.4287	1.0929	120.4	0.0	
CCSD/TZ2P	1.4073	1.0827	120.6	15.2	21.7
	1.4139	1.0819	120.5	0.0	
CCSD/cc-pVTZ	1.4022	1.0804	120.6	16.0	27.0
	1.0940	1.0794	120.5	0.0	
CCSD(T)/DZP	1.4253	1.0950	120.5	16.7	31.6
	1.4316	1.0940	120.4	0.0	
CCSD(T)/TZ2P	1.4058	1.0849	120.6	20.2	69.8
	1.4178	1.0833	120.5	0.0	
CCSD(T)/cc-pVTZ	1.4004	1.0827	120.6	21.0	82.5
	1.4132	1.0809	120.4	0.0	
B3LYP/DZP	1.4079	1.0949	120.9	26.8	271.6
	1.4295	1.0920	120.6	0.0	
B3LYP/TZ2P	1.3891	1.0884	121.1	28.4	354.6
	1.4153	1.0848	120.7	0.0	
B3LYP/cc-pVTZ	1.3880	1.0892	121.2	28.7	378.4
	1.4146	1.0854	120.7	0.0	
QCISD(T)/6-311G(d,p)	1.414	1.092	120.7	20.2	103.7[c]
	1.425	1.091	121.9	0.0	
experimentally derived[d]	1.405	1.091	121.8	25	233.9

[a] Bond lengths are in angstroms, angles are in degrees, and the barrier is in wavenumbers. [b] For each level of theory, the first line contains the data for the equilibrium geometry and the second line contains the data for the planar transition state. [c] Salhi-Benachenhou et al.[9] obtained the barrier to planarity using QCISD(T)/6-311++G(2df,p) at the QCISD(T)/6-311G(d,p) geometry. [d] Köppel et al.[1]

3. Results and Discussion

3.1. Geometry Analysis. The geometrical parameters of the equilibrium structure of ethylene radical cation and the barrier to planarity with respect to the constrained planar transition state are presented in Table 1. For all theoretical methods employed in this study, a substantial change in the optimized geometry occurs upon going from a double-ζ quality basis set with a single set of polarization functions to a triple-ζ quality basis set with two sets of polarization functions: r_{CC} decreases by ~0.02 Å, r_{CH} decreases by ~0.01 Å, θ_{HCC} increases by ~0.1°, and τ changes by as little as 1.6° for B3LYP and as much as 10.3° for MP2. The only major change in geometry that occurs upon adding f functions to the carbon atoms and d functions to the hydrogen atoms (i.e., going from the TZ2P basis to the cc-pVTZ basis) is the change in τ, which increases by 2.2° at the MP2 level. In general, our results show that r_{CC} and r_{CH} contract, θ_{HCC} is nearly static, and both the torsion angle and the barrier to planarity increase as the basis set is improved and/or as the amount of dynamical correlation energy recovered is increased from MP2 to CCSD to CCSD(T).

Presumably, cc-pVTZ should be the best basis set for both B3LYP and CCSD(T). Whereas the CCSD(T) geometry approaches that of Köppel and co-workers as the size of the basis set is increased, the B3LYP results move further away. The

TABLE 2: Valence Focal-Point Analysis of the Barrier to Planarity (cm^{-1}) of Ethylene Radical Cation[a]

	ΔE_e(UHF)	δMP2	δCCSD	δCCSD(T)	δCCSDT	δ[Q][b]	ΔE_e(CCSDT[Q])
cc-pVDZ (76)[c]	−281	+219	+32	+58	+18	−2	+44
cc-pVTZ (116)	−290	+256	+29	+67	+19	[−2]	[+61]
cc-pCVTZ (142)	−290	+273					
aug-cc-pVTZ (182)	−283	+277	+29	+69	[+19]	[−2]	[+92]
cc-pVQZ (230)	−291	+270	+29	+71	[+19]	[−2]	[+78]
cc-pCVQZ (288)	−290	+286					
aug-cc-pVQZ (344)	−289	+272	[+29]	[+71]	[+19]	[−2]	[+100]
cc-pV5Z (402)	−291		[+29]	[+71]	[+19]	[−2]	[+100]
aug-cc-pV5Z (574)	−291		[+29]	[+71]	[+19]	[−2]	[+100]
extrapolation limit (∞)	[−291]	[+274]	[+29]	[+71]	[+19]	[−2]	[+100]

[a] The value in brackets under ΔE_e(UHF) is the average of the barrier obtained by fitting eq 1 to the cc-pV(3,4,5)Z and aug-cc-pV(3,4,5) Hartree−Fock energies. The value in brackets under δMP2 is the average of the barrier obtained by fitting eq 2 to the cc-pV(3,4)Z and aug-cc-pV(3,4) MP2 energies. All of the values in brackets under the coupled-cluster columns were obtained by assuming that the basis set has been saturated for the given correction, i.e., a given method with a large basis set will yield the same contribution to the barrier as the given method with a smaller basis set. [b] The contribution of the quadruple excitations to the barrier is determined by δB-CCD(TQ) − δB-CCD(T). [c] Numbers in parentheses are the numbers of contracted Gaussian functions in the given basis sets.

B3LYP/cc-pVTZ geometry contracts r_{CC} by 0.012 Å and overestimates the torsion angle by 7.7° with respect to the CCSD(T)/cc-pVTZ geometry. The experimentally derived geometry of Köppel et al.[1] is between the B3LYP/cc-pVTZ and CCSD(T)/cc-pVTZ results. The QCISD(T)/6-311G(d,p) results of Salhi-Benachenhou et al.[9] compare well with our CCSD(T)/cc-pVTZ results, although r_{CC} differs by 0.01 Å.

Overall, the B3LYP/cc-pVTZ and CCSD(T)/cc-pVTZ geometries are similar and exemplify the expected change of removing a π-bonding electron from neutral ethylene (r_{CC} 1.339 Å, r_{CH} 1.086 Å, θ_{HCC} 124.8°).[39] The more pressing issue is the magnitude of the barrier to planarity considering the dramatic differences between the experimentally derived barrier, the Salhi-Benachenhou QCISD(T)/6-311++G(2df,p) barrier, and our B3LYP/cc-pVTZ and CCSD(T)/cc-pVTZ values for the barrier.

3.2. Barrier to Planarity. Although the barrier to planarity is rather small, probably less than 400 cm^{-1}, we attempted to make as accurate a determination as is possible at this time. Previous theoretical determinations of the barrier utilized standard Pople basis sets, and even though high-level theoretical methods [i.e., QCISD(T) and CCSD(T)] were also utilized, no attempt was ever made to estimate the ab initio limit of the barrier, which can be achieved through schemes similar to Allen's focal-point analysis.[40]

Feller[17] has shown that the lowering of the Hartree−Fock energy exhibits an exponential convergence with respect to the cardinal number X of the Dunning correlation-consistent basis sets

$$E_X = E_{\mathrm{CBS}} + a\mathrm{e}^{(-bX)} \tag{1}$$

The extrapolated Hartree−Fock barrier obtained by fitting eq 1 to the cc-pV(3,4,5)Z HF energies is −291.4 cm^{-1} (see Table 2). The difference between the cc-pV(3,4,5)Z and aug-cc-pV(3,4,5)Z extrapolated Hartree−Fock barriers is only 0.3 cm^{-1}, thus showing that the Hartree−Fock basis set limit has been converged to within 1 cm^{-1}.

The extrapolation of the correlation energy uses a two-point inverse-power scheme proposed by Helgaker, Klopper, Koch, and Noga[18]

$$E_{\mathrm{CBS}}(X,Y) = \frac{E^X X^3 - E^Y Y^3}{X^3 - Y^3} \tag{2}$$

where E^X and E^Y denote the correlation energies obtained from correlation-consistent basis sets with cardinal numbers X and Y, respectively. The cc-pV(3,4)Z MP2 contribution is estimated at +279 cm^{-1}, still not enough to stabilize the twisted structure. The addition of diffuse functions stabilizes the planar transition state by 11 cm^{-1}. Yet, the bulk of the total electronic barrier is due to higher-order electron correlation effects. The CCSD and CCSD(T) results do show a stabilizing effect for the twisted conformation, contributing an additional +29 and +71 cm^{-1}, respectively. The CCSDT results provide a +19 cm^{-1} contribution, still a considerable portion of the total. The correlation energy from quadruple excitations [Q] contributes only −2 cm^{-1}, thus suggesting that quadruple and higher excitations contribute very little to the barrier.

The core correlation contribution was determined by subtracting the frozen-core MP2/cc-pCVQZ contribution from the all-electron MP2/cc-pCVQZ contribution, which yielded a core correlation contribution of +16 cm^{-1}. To reach a final estimate of the barrier to planarity, the valence contribution was added to the core correlation contribution. The relativistic treatment of including the mass-velocity and one-electron Darwin terms adds less than 1 cm^{-1} to the magnitude of the barrier. The two-electron Darwin term, the spin−orbit interaction, and the non-Born−Oppenheimer correction were neglected; however, these effects should be smaller than the estimated uncertainty in the final barrier to planarity. We also include the possible error in the magnitude of the barrier due to basis-set truncation and neglect of higher-order correlation. The basis-set-truncation error was estimated by the difference between contributions to the barrier from the cc-pVXZ and aug-cc-pVXZ series of basis sets, and the neglect of higher-order correlation was estimated by the reduction in the contribution to the barrier from the UHF → MP2 → CCSD → CCSD(T) → CCSDT → [Q] series. Given the small contribution from [Q], we estimate that the effect of higher-order correlation contributions is probably less than 10 cm^{-1}. The final vibrationless barrier to planarity is (100 + 16) ± (25 + 10) = 116 ± 35 cm^{-1}.

3.3. Vibrational Analysis. The calculated harmonic vibrational frequencies of the cation are reported in Table 3. Our primary emphasis is on the second, third, fourth, and seventh modes as we have experimental and theoretical data for comparison.

The results of previous theoretical determinations of the harmonic vibrational frequencies started from a D_{2h} reference geometry, even though the cation is now established to have D_2 symmetry at equilibrium. Another problem encountered in previous theoretical studies was that the highest level of theory used was the Hartree−Fock method. Hartree−Fock theory is known to overestimate the vibrational frequencies, although

TABLE 3: Harmonic Vibrational Frequencies (cm^{-1}) of the Ethylene Radical Cation[a]

symmetry	B3LYP/cc-pVTZ	CCSD(T)/DZP	CCSD(T)/TZ2P	CCSD(T)/cc-pVTZ	other
ω_1(a)	3082 (0)	3168 (0)	3133 (0)	3149 (0)	
ω_2(a)	1502 (0)	1563 (0)	1550 (0)	1557 (0)	1510[b]
ω_3(a)	1273 (0)	1275 (0)	1269 (0)	1290 (0)	1264[b]
[ω_4(a)][c]	[616] (0)	[328] (0)	[402] (0)	[420] (0)	887[d]
ω_5(b$_1$)	3176 (3)	3284 (1)	3243 (2)	3229 (2)	
ω_6(b$_1$)	1206 (11)	1229 (7)	1240 (11)	1237 (13)	
ω_7(b$_1$)	887 (37)	944 (74)	943 (69)	955 (70)	908[e]
ω_8(b$_2$)	3196 (84)	3300 (80)	3261 (108)	3249 (110)	
ω_9(b$_2$)	1078 (1)	1069 (0)	1110 (1)	1122 (1)	
ω_{10}(b$_2$)	785 (5)	819 (7)	822 (8)	815 (9)	
ω_{11}(b$_3$)	3086 (87)	3160 (69)	3129 (90)	3143 (91)	
ω_{12}(b$_3$)	1432 (55)	1467 (62)	1470 (71)	1472 (76)	

[a] Values in parentheses are the infrared intensities in km mol^{-1}. [b] Experimentally derived harmonic frequencies from Pollard et al.[14] [c] The ω_4 mode is anharmonic and should not be estimated with a harmonic potential. [d] Köppel et al.[1] [e] Draves et al.[16]

Somasundram and Handy[15] scaled their results with ($\omega_{\mathrm{expt}}/\omega_{\mathrm{calc}}$) for the neutral to compensate for basis-set incompleteness and neglect of higher-order correlation effects.

The four levels of theory used for determining the harmonic vibrational frequencies are (B3LYP/cc-pVTZ, CCSD(T)/DZP, CCSD(T)/TZ2P, CCSD(T)/cc-pVTZ), all at their respectively optimized geometries. The CCSD(T)/(DZP, TZ2P, cc-pVTZ) level of theory was chosen for two reasons. First, the computational cost of determining the harmonic vibrational frequencies with the CCSD(T) method and a larger basis set is beyond our reach. Second, Thomas et al.[41] performed a systematic study on the accuracy of CCSD(T) with these three basis sets. Their study provided approximate scaling factors of (2.4, 2.3, 2.2)% for the CCSD(T)/(DZP, TZ2P, cc-pVTZ) harmonic vibrational frequencies, respectively. The density functional results are included for comparison with the CCSD(T) results.

The harmonic frequency of the C$-$C stretching mode, ω_2(a), was experimentally derived by Pollard et al.[14] All four levels of theory compare very well with the experimentally derived harmonic frequency, with unscaled values varying by (-8, $+53$, $+40$, $+47$) cm^{-1} and scaled CCSD(T) values varying by ($+15$, $+4$, $+13$) cm^{-1} from experiment. The harmonic frequency of the H$-$C$-$H bending mode, ω_3(a), also agrees very well with the experimentally derived harmonic frequency, with unscaled values varying by ($+9$, $+11$, $+5$, $+26$) cm^{-1} and scaled CCSD(T) values varying by (-20, -24, -2) cm^{-1} from experiment.

The fourth vibrational mode, ω_4(a), is a torsion mode and is highly sensitive to the optimized torsion angle as well as the level of theory. Pollard and co-workers did measure the $2\nu_4 = 441 \pm 4$ cm^{-1} transition and noted that the (0001) transition is too weak to be observed in the 21.2 eV PES, even with observed resolution of 12$-$13 meV fwhm. The harmonic frequency of the ω_4(a) mode is more than 5 times the height of the barrier to planarity at the CCSD(T)/cc-pVTZ level of theory. We followed the procedure of Valeev and co-workers[42] for determining the bound eigenstates of a one-dimensional potential: the Mathematica package[43] was used to evaluate the $G(\tau,\tau)$ matrix element along the torsional path, to construct an interpolating function for the CCSD(T)/cc-pVTZ potential, and to apply the Cooley$-$Numerov procedure[44] for determining the exact torsional eigenstates, although the splitting of energy levels due to the ~10 500 cm^{-1} barrier at $\tau = 90°$ was neglected. The first five energy levels were determined to be $\epsilon_\tau = (122, 324, 688, 1093, 1545)$ cm^{-1}. Assuming the torsion mode does not couple to any other vibrational modes, the fundamental transition and the first three overtones are $G(\nu_4) = (202, 566, 971, 1423)$ cm^{-1} compared to Pollard's experimentally derived values of $G(\nu_4)$ = ([not observed], 438, 766, 1158) cm^{-1}. At the CCSD(T)/cc-pVTZ level of theory, the ground vibrational state is above the barrier to planarity (82.5 cm^{-1} from Table 1); thus, one has to consider the possibility that the ethylene radical cation is a quasiplanar molecule with a large-amplitude torsional motion. However, as the previous section of the paper has shown, the estimated ab initio limit of the barrier to planarity is 116 ± 35 cm^{-1}. Therefore, to reach a definitive conclusion as to the nature of the lowest vibrational energy level due to the low energy barrier, the torsion potential must be determined using methods approaching the ab initio limit, which is currently beyond our capability. Köppel and co-workers used 887 cm^{-1} for ω_4 (see Table 3) in their empirical vibronic coupling model; however, our results show that the fundamental transition of the fourth vibrational mode is approximately 200 cm^{-1}.

Our motivation for determining the harmonic vibrational frequencies of the cation was to aid in the assignment of the infrared cavity-ring-down spectrum of Draves and Taylor.[16] Their results showed a two-peak signature that was duly assigned to the ω_7(b$_1$) CH$_2$ wag. The second peak was assigned as the first overtone with an anharmonicity ($\omega_e x_e$) of ~9 cm^{-1}. From their analysis, they determined that the harmonic ω_7(b$_1$) frequency is ~908 cm^{-1}. Using the unscaled and scaled results, theory and experiment are in agreement to within (2.4, 3.8, 3.7, 4.9)% and (1.4, 1.4, 2.8)%, respectively.

4. Conclusions

The following conclusions can be drawn from the results presented in this study:

(1) The CCSD(T)/cc-pVTZ equilibrium geometry compares well with the results of Salhi-Benachenhou et al.,[9] although r_{CC} contracts by 0.005 Å and τ decreases by 4.0° compared to Köppel et al.'s experimentally derived values.[1]

(2) The barrier to planarity has been estimated using a series of methods and basis sets designed to extrapolate to the ab initio limit. The final vibrationless barrier of 116 ± 35 cm^{-1} is the result of the most systematic and comprehensive examination of this barrier to date.

(3) The B3LYP harmonic vibrational frequencies are more accurate than the unscaled CCSD(T) harmonic vibrational frequencies, although both the B3LYP and the scaled CCSD(T) harmonic vibrational frequencies compare very well with the experimental results of Pollard[14] and Draves and Taylor.[16]

(4) Exact torsion vibrational energy levels evaluated at the CCSD(T)/cc-pVTZ level of theory, neglecting mode coupling, all lie above the barrier to planarity. A definitive conclusion of the torsion vibrational mode will require a torsion potential approaching the ab initio limit, including mode coupling, which is currently beyond our capability.

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