Semispectroscopic and Quantitative Structure−Property Relationship Estimates of the Equilibrium and Vibrationally Averaged Structure and Dipole Moment of 1-Buten-3-yne

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Systematic quantum chemical calculations have been performed to obtain precise estimates of the equilibrium and vibrationally averaged molecular structure and electric dipole moment of vinylacetylene (VA, 1-buten-3-yne). Anharmonic (cubic and semi-diagonal quartic) MP2/cc-pVTZ force fields in normal coordinates were computed to account for anharmonic vibrational effects, including zero-point contributions to the rotational constants and the electric dipole moment. A simultaneous weighted least-squares structural refinement was performed, resulting in the best semispectroscopic estimate of the r_e structure of VA. The refinement was based on experimentally measured ground-state rotational constants of two isotopologs of VA corrected to equilibrium values using MP2/cc-pVTZ vibration−rotation interaction constants and all-electron CCSD(T)/ aug-cc-pVTZ structural constraints. The semispectroscopic r_e structure of VA agrees excellently with the high-level CCSD(T)/aug-cc-pVTZ ab initio structure. The most dependable, CCSD(T)/cc-pVQZ//CCSD(T)/ aug-cc-pVTZ equilibrium electric dipole moment of VA, in D, is $\mu_a = 0.4088$, $\mu_b = 0.0004$, and $\mu_c = 0$. The vibrationally corrected *a*-component of 0.4214 D is in excellent agreement with one of the available experimental values. The present analysis shows that μ_b is negligible even after vibrational correction. A simple quantitative structure−property relationship (QSPR) model resulted in a highly similar estimate, 0.45 D, for the electric dipole moment of VA.

I. Introduction

Microwave (MW) spectroscopy is possibly the best experimental tool for determining reliable gas-phase molecular structures and dipole moments (DM) of small to medium-sized molecules.[1−4] Not only the structure itself but also the permanent electric DM is an important property as they provide fundamental information concerning the electronic structure of molecules. Generally, experimentally determined structures and dipole moments refer to vibrational averages of the equilibrium values.

Some time ago one of us studied[5,6] the permanent electric dipole moments of aliphatic hydrocarbons at ab initio Hartree−Fock (HF),[7] second-order Møller−Plesset perturbation theory (MP2),[8,9] and B3LYP density functional theory (DFT)[10,11] levels. It was found that even these introductory levels of electronic structure theory (e.g., HF/6-311G**//MP2(FC)/6-311G** and B3LYP/6-311G**) resulted in reliable estimates of DMs, where 6-311G** is an almost triple-ζ quality split-valence basis,[12] FC (frozen core) in parentheses means that the inner-shell electrons were excluded from the electron correlation treatment, and // stands for "at the geometry of". Furthermore, on the basis of the computed results, the following qualitative observations were made:[5,6] (i) in alkanes, the methyl group is electron-withdrawing relative to the methylene group, i.e., the methyl group is at the negative end of the molecule; (ii) in alkenes and alkynes, the alkyl group constitutes the positive end of the molecule; and (iii) the ethynyl group is electron-withdrawing relative to the

vinyl group. It is worth mentioning that recent measurements by photoelectron spectroscopy[13] provided further evidence for the validity of (i) and (ii). For molecules with conjugate C=C double and C≡C triple bonds, e.g., 1-buten-3-yne, 1-penten-3-yne, *cis*-3-penten-1-yne, *trans*-3-penten-1-yne, and 2-methyl-1-buten-3-yne, the B3LYP dipole moments were closer to the experimental ones than the HF dipole moments.[6] The situation was the reverse for molecules containing conjugate C=C double bonds.[5] Among the molecules studied, 1-buten-3-yne (vinyl-acetylene, VA) is the smallest molecule with conjugate C=C double and C≡C triple bonds. VA is a common product of hydrocarbon pyrolysis and oxidation[14] and may be an abundant species in space.[15] Experimental results, obtained by gas electron diffraction (GED),[16,17] microwave (MW) spectroscopy,[18−21] and vibrational spectroscopy,[21] are available in the literature to elucidate its structural and electronic properties. In fact, three different values are available as experimental vibrationally averaged μ_0 dipole moments of VA: 0.44 D,[18] 0.4 D,[22] and 0.22 D.[19] The most recent experimental value of 0.22 D is precisely half of the oldest one, 0.44 D. In contrast, DFT studies[6,15] support the higher value of about 0.4 D. However, it may be argued that the success of introductory ab initio and DFT methods arises from a fortuitous error cancellation and thus the computational support of the higher value for the DM of VA is not conclusive.

With the help of sophisticated quantum chemical (QC) methods, it has become possible to obtain precise equilibrium, r_e, structures for relatively small, isolated molecules not only from experiment but also from theory. For recent successes of electronic structure theory in determining accurate structures for relatively sizable molecules, see refs 23 and 24. The same

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TABLE 1: Total Energies (in E_h) and Selected Born−Oppenheimer Equilibrium Structural Parameters (Bond Lengths in Angstroms and Angles in Degrees) of the Vinylacetylene Molecule at the RHF, MP2, CCSD, and CCSD(T) Levels of Theory[a]

method	total energy	C−C	C=C	C≡C	C=C−C
RHF/aug-cc-pV5Z (828)	−153.777958	1.4359	1.3174	1.1822	123.77
MP2/aug-cc-pVQZ (504)	−154.554900	1.4171	1.3348	1.2118	123.43
MP4(SDQ)/cc-pVTZ (176)	−154.473919	1.4263	1.3314	1.2032	123.90
CCSD/aug-cc-pVTZ (276)	−154.493517	1.4251	1.3310	1.2026	123.73
CCSD(T)/aug-cc-pVTZ (276)	−154.528756	1.4241	1.3384	1.2102	123.74
expt[16,b]		1.430	1.335	1.206	123.4
expt[17,b]		1.4310	1.3416	1.2086	123.1

[a] The number of contracted Gaussian functions is given in parentheses. All ab initio structures have been fully optimized to at least the number of digits presented for the structural parameters. [b] See the original publications for the definitions employed for obtaining these experimental vibrationally averaged structural data.

high precision is true for dipole moments; see ref 25. Therefore, it is clear that definitive structures and dipole moments can be derived by a judicious combined use of experimental and theoretical information on VA.

Besides the ab initio and DFT methods of electronic structure theory, there is an interesting nonquantum-mechanical alternative for studying dipole moments, the quantitative structure−property relationship (QSPR). The QSPR methodology derives topological indices from the bonding pattern of molecules and then tries to make correlations between these indices and diverse molecular properties.[26,27] Recently, dipole moments of various hydrocarbon molecules were calculated by means of correlation weighting of local graph invariants within the context of QSPR theory.[28,29]

In the present investigation, various high-quality QC models with extended basis sets are employed to obtain precise estimates of the equilibrium molecular structure and permanent electric dipole moment characterizing the ground electronic state of VA. To account for anharmonic vibrational effects, including total zero-point contributions to rotational constants and electric dipole moment, an anharmonic (cubic and semi-diagonal quartic) vibrational force field is computed. With the help of our best theoretical equilibrium geometry, a weighted least-squares refinement is performed to determine a reliable empirically based semispectroscopic r_e structure of VA. Our definitive vibrationally corrected estimate for the electric dipole moment of VA is compared with the available experimental data. In addition, a simple QSPR model[29] is employed to produce an estimate for the electric dipole moment of VA.

II. Computational Details

Complete geometry optimizations for VA in its ground electronic state were performed at various levels of electronic structure theory: restricted Hartree−Fock (HF),[7] second-order Møller−Plesset (MP2),[8,9] fourth-order Møller−Plesset with single, double, and quadruple substitutions (MP4(SDQ)),[30] coupled-cluster (CC) with single and double excitations (CCSD),[31−34] and CCSD augmented with perturbative triple excitations (CCSD(T)).[35,36] Unless indicated otherwise, all electrons were included in the electron correlation treatments employing the RHF solution as reference. In every case the optimized ground-state geometry of VA possessed C_s point-group symmetry, as checked by second-derivative calculations in the simpler cases.

The atomic orbital basis sets employed included Pople-type (split-valence) basis sets[12] and Dunning-type (correlation consistent, cc) basis sets, in the latter case (aug-)cc-pVXZ, with $X = 2(D), 3(T), 4(Q),$ and $5.$[37] The cc basis sets are especially useful as they facilitate extrapolation to the complete basis set (CBS) limit.[38−40]
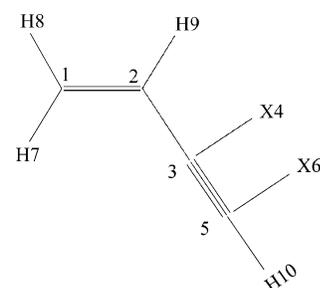
Figure 1. Structure and atomic numbering of 1-buten-3-yne.

TABLE 2: Geometric Constraints of VA Used during Fitting of the Final Semispectroscopic Structure[a]

$r(2,3) - r(1,2) = 0.0857$	$\theta(3,2,1) - \theta(7,1,2) = 2.69$
$r(2,3) - r(3,5) = 0.2139$	$\theta(7,1,2) - \theta(8,1,2) = 0.37$
$r(1,7) - r(1,8) = 0.0008$	$\theta(8,1,2) - \theta(9,2,1) = 0.93$
$r(2,9) - r(1,8) = 0.0023$	$\theta(10,5,6) - \theta(5,3,4) = 1.06$
$r(2,9) - r(5,10) = 0.0208$	

[a] All constraints are based on CCSD(T)/aug-cc-pVTZ optimized structure. Units are angstroms for distances (r) and degrees for bond angles (θ). See Figure 1 for labeling of the atoms.

To help account for anharmonic vibrational effects in the ground-state MW rotational constants and in the permanent electric dipole moment, a cubic (and a semidiagonal quartic) force-field expansion of the vibrational potential of VA was determined in normal coordinates at the MP2/cc-pVTZ level, employing finite differences of tightly converged analytic second derivatives.[41]

The Gaussian98,[42] Dalton,[43] PSI3,[44] and ACESII[45] program systems have been employed for the electronic structure computations of this study. Anharmonic normal coordinate force fields for the isotopologs of VA considered were obtained with facilities provided by the ACESII program system.[45] A newly developed FORTRAN program, SemiGeo, was used for refinement of the semispectroscopic structure.

III. Results and Discussion

Table 1 lists at all levels of theory employed the best calculated and the experimental structural parameters for the carbon skeleton of VA (for the structure of VA, see Figure 1). All the data used for the structural refinement of VA to derive a new semispectroscopic r_e molecular structure are given in Tables 2 and 3. Table 4 contains the geometric parameters of the fitted semispectroscopic r_e molecular structure of VA, together with those of the CCSD(T)/aug-cc-pVTZ optimization. Table 5 lists the equilibrium dipole moments computed at various levels of theory. Finally, Tables S6−S9 in the Supporting Information contain a large number of total electronic energies and optimized geometries using different basis sets at the RHF (Table S6), MP2 (Table S7), MP4(SDQ) (Table S8), CCSD (Table S9), and CCSD(T) (Table S9) levels of theory.

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TABLE 3: Experimental Ground-State Rotational Constants of Two Isotopologs of VA and Their Equilibrium Counterparts, All in MHz[a]

rotational constants	parent	1-buten-3-yne-4d
A_0	50308.(55)	49393.(34)
B_0	4744.9317(77)	4403.9538(40)
C_0	4329.7899(77)	4037.8007(40)
A_e	50493.8574	49559.1928
B_e	4756.4640	4413.2089
C_e	4347.1136	4052.4082

[a] Experimental values from ref 21. The ground-state rotational constants have been corrected by MP2/cc-pVTZ vibration−rotation interaction constants to arrive at equilibrium values.

TABLE 4: Structural Parameters for VA[a]

	r_e(fit)	CCSD(T)/aug-cc-pVTZ
$r(1,2)$	1.3382(10)	1.3384
$r(2,3)$	1.4239(7)	1.4241
$r(3,5)$	1.2100(13)	1.2102
$r(1,7)$	1.0796(27)	1.0797
$r(1,8)$	1.0787(23)	1.0789
$r(2,9)$	1.0810(17)	1.0811
$r(5,10)$	1.0602(7)	1.0603
$\theta(3,2,1)$	123.62(7)	123.74
$\theta(7,1,2)$	120.93(11)	121.05
$\theta(8,1,2)$	120.55(13)	120.67
$\theta(9,2,1)$	119.63(16)	119.75
$\theta(5,3,4)$	88.96(5)	89.22
$\theta(10,5,6)$	90.02(4)	90.29

[a] See Figure 1 for labeling of the atoms. Units are angstroms for distances (r) and degrees for bond angles (θ). The estimated standard errors of the geometric parameters are given in parentheses.

TABLE 5: Theoretical Predictions of the Total μ_e Dipole Moment, in Debye, for the Vinylacetylene Molecule at Various Levels of Theory[a]

basis set	HF	MP2	MP4(SDQ)	CCSD	CCSD(T)
6-31G* (68)	0.4707	0.3009	0.3504	0.3550	
6-311G* (84)	0.5118	0.3431	0.3889	0.3920	
6-311G** (96)	0.5256	0.3295	0.3754	0.3806	
6-311++G** (116)	0.5394	0.3437	0.3874	0.3937	
6-311++G(2d,2p) (148)	0.5421	0.3663	0.4076	0.4123	
6-311++G(3df,3pd) (228)	0.5361	0.3634		0.4121	
cc-pVDZ (76)	0.5087	0.3221	0.3710	0.3776	0.3649
cc-pVTZ (176)	0.5326	0.3633	0.4093	0.4142	0.4008
cc-pVQZ (340)	0.5366	0.3731			0.4088[b]
cc-pV5Z (584)	0.5334				
aug-cc-pVDZ (128)	0.5471	0.3588	0.4034	0.4123	0.4026
aug-cc-pVTZ (276)	0.5315	0.3617		0.4126	0.4002
aug-cc-pVQZ (504)	0.5323	0.3708			
aug-cc-pV5Z (828)	0.5322				

[a] The number of contracted Gaussian functions is given in parentheses. [b] CCSD(T)/cc-pVQZ//CCSD(T)/aug-cc-pVTZ.

III.1. Empirical Structures. More than fifty years ago Bastiansen,[16] from GED measurements, obtained some structural parameters for the carbon skeleton of VA. Later, on the basis of a careful joint analysis of GED and MW measurements, Fukuyama and co-workers[17] derived an average (r_{av}) molecular structure.[17] Generally, it is difficult to determine the positions of hydrogen atoms by means of MW spectroscopy[1] and a number of constraints were applied in the evaluation of the positions of the hydrogen atoms in VA.[17] Therefore, only the structure of the carbon skeleton will be considered when published experimental data are compared to the calculated ones in what follows.

As Table 1 shows, the two experimental structures,[16,17] except for the C=C double bond, are close to each other. All three CC bonds were determined to be slightly longer by Fukuyama

and co-workers:[17] the differences for the CC single, double, and triple bonds are 0.001, 0.0066, and 0.0026 Å, respectively, which might result from the different definitions of these distances in the two studies. It should also be kept in mind that GED distances (both r_a and r_g) are inherently substantially longer than their equilibrium counterparts, r_e, due to vibrational averaging effects. The deviation of the C=C−C bond angles is within the reported experimental uncertainties.

It is worth comparing the lengths of the CC bonds of VA to those of the isolated CC bond prototypes in ethane, ethene, and ethyne. Harmony[46,47] has determined the equilibrium CC bond lengths for these molecules as 1.522 Å (ethane), 1.332 Å (ethene), and 1.203 Å (ethyne). In light of the prototypical data and the previous discussion, it can be concluded that the empirical molecular geometry of VA published by Fukuyama and co-workers[17] appears to be somewhat more reliable than that of Bastiansen.[16] Therefore, for comparison with the computed results, the experimental geometry of Fukuyama and co-workers is used as a reference in what follows.

III.2. Computed Structures. According to Tables 1 and S6, the C−C single bond is too long, whereas both the C=C double and C≡C triple bonds are too short at the RHF level of theory. This reveals that this introductory level of electronic structure theory underestimates the conjugation between the C=C double and C≡C triple bonds. The calculated CC bond lengths are gradually decreasing with the size of the basis set applied, approaching the following well-defined CBS limits: 1.436 Å (C−C), 1.317 Å (C=C), and 1.182 Å (C≡C). In contrast, the calculated C=C−C bond angle is rather insensitive to the size of the basis set and is slightly larger than the experimental value.

At the MP2 level of theory all three CC bond lengths are decreasing with increasing basis set size (see Tables 1 and S7). With the largest basis set applied, which is aug-cc-pVQZ, the C−C single bond is too short, and the values of the remaining parameters are close to their experimental counterparts. Tables 1 and S8 show that the situation is slightly better at the MP4 level of theory. However, the C=C double and C≡C triple bonds are too short.

As to the CCSD and CCSD(T) equilibrium geometries, all three CC bond lengths are decreasing with the increase in the basis, steadily approaching the experimental values (see Tables 1 and S9). At the CCSD/6-311++G(3df,3pd) level of theory (Table S9), the differences for the CC single, double, and triple bonds are +0.0009, +0.0079, and +0.0046 Å, respectively. The same differences are +0.0069, +0.0032, and −0.0016 Å for the CCSD(T)/aug-cc-pVTZ equilibrium geometry. These data reveal that, as expected, in this study the CCSD(T)/aug-cc-pVTZ level provides the best estimate for the equilibrium geometry of VA. Due to conjugation, the C−C single bond is shortened by 0.0979 Å, whereas the C=C and C≡C bonds are lengthened by 0.0064 and 0.0072 Å, respectively, relative to the prototypical isolated values[46,47] determined by Harmony. Interestingly, the lengthening is larger for the C≡C triple bond than for the C=C double bond.

III.3. New Semispectroscopic Structure. Following the recipe of ref 24, and using the newly developed SemiGeo program, written in Fortran, which is similar in capability to the MolStruct program,[24] a constrained parameter estimation via the weighted least-squares method[48] was performed to obtain a reliable empirically based, semispectroscopic r_e structure for VA. The robust simplex method[49] with error analysis[50] has been implemented in the program. SemiGeo can be used either for unconstrained or for constrained optimization through simultaneous weighted least-squares fitting.[51]

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The published experimental rotational constants[19−21] of two isotopologs of VA (parent and 1-buten-3-yne-4d, see Figure 1 for atom labeling) are insufficient to derive an r_e structure without the imposition of numerous constraints. To wit, there are 13 geometric degrees of freedom for VA within the C_s point-group symmetry, but only 6 empirical rotational constants are available. However, we can impose reliable constraints with the help of the CCSD(T)/aug-cc-pVTZ optimum structure. After extensive testing, it was found that the 9 CCSD(T)/aug-cc-pVTZ structural constraints shown in Table 2 are the most meaningful both physically and statistically.

The zero-point vibrational corrections for the ground-state rotational constants were calculated from the cubic normal coordinate force field at the MP2/cc-pVTZ level of theory as the appropriate sum of vibration−rotation constants, and they were then added to the empirical ground-state rotational constants. Table 3 lists the experimental ground-state MW rotational constants[21] and their corrected equilibrium counterparts. The quality of this correction is supported by the diminutive remaining inertial defect, $\Delta = I_c - I_a - I_b$, which is −0.003 (−0.002) u Å² for the estimate of the equilibrium moments of inertia of the parent (1-buten-3-yne-4d) isotopolog whereas the measured ground-state one is 0.166 (0.174) u Å².

To obtain reliable semispectroscopic r_e parameters for VA, a large number of constrained optimizations were performed. The one judged the best had structural constraints reported in Table 2. The corrected empirical equilibrium rotational constants can be fitted well, the weighted root-mean-square (rms) error is only 0.014₃ MHz, no residual is over 0.08 MHz, and all the correlation coefficients are in the interval [−0.91, 0.86]. As can be seen from Table 4, there is excellent agreement between the semispectroscopic r_e(fit) values and the best theoretical predictions. Generally, the discrepancies are within the estimated standard errors.

Therefore, any molecular property, including the dipole moment, computed at the CCSD(T)/aug-cc-pVTZ optimum structure, approximating the true equilibrium structure of VA extremely well, should not suffer from any hidden structural effects.

III.4. Dipole Moment from QSPR Theory. Recently, several molecular topological indices have been introduced for reproducing the dipole moments of various hydrocarbon molecules.[29] These indices are calculated from 2-dimensional molecular bonding patterns and they are defined by the following equation:

$$DCW(a_k, LI_k) = \sum_{k=1}^{N} CW(a_k) \times CW(LI_k)$$

where a_k and $CW(a_k)$ are the kth vertex of the labeled hydrogen filled molecular graph and its correlation weight, respectively. LI_k stands for the local graph invariant and $CW(LI_k)$ represents its correlation weight. For instance, the number of paths of length two (pt2) starting from the kth vertex can be regarded as a local graph invariant. Assuming linear correlation between the DM values and the $DCW(a_k, pt2_k)$ indices, a Monte Carlo method was applied to derive optimal correlation weights for a training set of selected molecules. The details are to be found in ref 29. It is worth mentioning that no molecules with conjugate C=C double and C≡C triple bonds were either in the training set or in the whole set of the molecules studied.

Using the optimal correlation weights of Castro and co-workers[29] yields the values 10.261 and 11.648 for the DCW-(a_k,pt2$_k$) indices of VA and 2-methyl-1-buten-3-yne (2MeVA),

respectively. The assumed linear relation between the DM values and the $DCW(a_k, pt2_k)$ indices results in

$$\mu(VA) = 10.261/11.648 \times \mu(2MeVA) =$$
$$0.881 \times \mu(2MeVA)$$

for the DM of VA. Substituting the well-established 0.513 D for the DM of 2-methyl-1-buten-3-yne[52] gives the value 0.45 D for the DM of VA. This value is about twice as large as the most recent experimental value;[19] however, it is very close to that published by Sobolev and co-workers (0.44 D).[18]

III.5. Ab Initio Dipole Moments of VA. Table 5 reveals that the RHF/CBS value for μ_e of VA is 0.53 D. In contrast, the MP2 value, 0.37 D, is too small relative to the QSPR estimate of 0.45 D. As far as the MP4(SDQ), CCSD, and CCSD(T) levels of theory are concerned, the estimated value for the μ_e dipole moment approaches a well-defined CBS limit of 0.41 D in each case. Therefore, ab initio calculations without exception support the higher value for μ_e of VA.

Our best estimate for the μ_e dipole moment of VA, $\mu_a = 0.4088$, $\mu_b = 0.0004$, and $\mu_c = 0$ D, was obtained from a CCSD(T)/cc-pVQZ//CCSD(T)/aug-cc-pVTZ calculation. It is clearly seen that the b-component is 1000 times smaller than the a-component; therefore it can be neglected. To facilitate direct comparison of the theoretical equilibrium value with the experimental μ_0 dipole moments,[18,19,22] zero-point vibrational contributions to the dipole moment were calculated at the MP2/cc-pVTZ level of theory, resulting in $\Delta\mu_a = 0.0126$, $\Delta\mu_b = 0.0008$, and $\Delta\mu_c = 0$ D. The vibrationally corrected a-component of 0.4214 D is in excellent agreement with the experimental value of 0.43(1) D of Sobolev and co-workers.[18] It is worth noting that Sobolev and co-workers estimated only the value of the b-component and derived an overall value of 0.44 D for the DM of VA. However, our analysis reveals that the b-component is negligible even after vibrational correction; therefore, the best experimental μ_0 dipole moment of VA is 0.43 ± 0.01 D, based on the measurements of Sobolev and co-workers.[18]

IV. Conclusions

Zero-point vibrational corrections to the ground-state rotational constants of vinylacetylene were derived from cubic MP2/cc-pVTZ force fields and were used to correct the empirical ground-state rotational constants of two isotopologs. A simultaneous weighted least-squares structural refinement afforded a new semispectroscopic r_e structure for VA. The refinement was based on the corrected experimental equilibrium rotational constants of two isotopologs and all-electron CCSD(T)/aug-cc-pVTZ structural constraints. Excellent agreement between the semispectroscopic r_e structure of VA and the highest-level CCSD(T)/aug-cc-pVTZ ab initio structure was found. Therefore, any molecular property, including the dipole moment, computed at the CCSD(T)/aug-cc-pVTZ optimum structure should not suffer from any hidden structural effects.

The QSPR estimate of the dipole moment of VA, 0.45 D, is about twice the most recent experimental value.[19] However, it is very close to an old value, 0.44 D, published by Sobolev and co-workers.[18] Our best estimate for the equilibrium dipole moment of VA, $\mu_a = 0.4088$, $\mu_b = 0.0004$, and $\mu_c = 0$ D, was derived from a CCSD(T)/cc-pVQZ//CCSD(T)/aug-cc-pVTZ calculation. The vibrationally corrected a-component of 0.4214 D is in excellent agreement with the experimental value[18] of 0.43(1) D of Sobolev and co-workers. Furthermore, our analysis reveals that the b-component is negligible even after

vibrational correction, and therefore the best experimental μ_0 dipole moment of VA is 0.43 ± 0.01 D, as measured by Sobolev and co-workers.[18]

Supporting Information Available: Tables S6–S9 showing the total energy and selected geometrical parameters for the vinylacetylene molecule at various (RHF, MP2, MP4(SDQ), CCSD, CCSD(T)) levels of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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