

# Complete basis set extrapolations for low-lying triplet electronic states of acetylene and vinylidene

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A recent study by Ahmed, Peterka, and Suits [J. Chem. Phys. **110**, 4248 (1999)] has presented the first experimentally derived estimate of the singlet–triplet gap in the simplest alkyne, acetylene. Their value,  $T_0(\tilde{a}^3B_2) = 28\,900\text{ cm}^{-1}$ , does not agree with previous theoretical predictions using the coupled-cluster singles, doubles, and perturbative triples [CCSD(T)] method and a triple- $\zeta$  plus double polarization plus  $f$ -function basis set (TZ2P $f$ ), which yields  $30\,500 \pm 1000\text{ cm}^{-1}$ . This discrepancy has prompted us to investigate possible deficiencies in this usually-accurate theoretical approach. Employing extrapolations to the complete basis set limit along with corrections for full connected triple excitations, core correlation, and even relativistic effects, we obtain a value of  $30\,900\text{ cm}^{-1}$  (estimated uncertainty  $\pm 230\text{ cm}^{-1}$ ), demonstrating that the experimental value is underestimated. To assist in the interpretation of anticipated future experiments, we also present highly accurate excitation energies for the other three low-lying triplet states of acetylene,  $\tilde{a}^3B_u$  ( $33\,570 \pm 230\text{ cm}^{-1}$ ),  $\tilde{b}^3A_u$  ( $36\,040 \pm 260\text{ cm}^{-1}$ ), and  $\tilde{b}^3A_2$  ( $38\,380 \pm 260\text{ cm}^{-1}$ ), and the three lowest-lying states of vinylidene,  $\tilde{X}^1A_1$  ( $15\,150 \pm 230\text{ cm}^{-1}$ ),  $\tilde{a}^3B_2$  ( $31\,870 \pm 230\text{ cm}^{-1}$ ), and  $\tilde{b}^3A_2$  ( $36\,840 \pm 350\text{ cm}^{-1}$ ). Finally, we assess the ability of density functional theory (DFT) and the Gaussian-3 method to match our benchmark results for adiabatic excitation energies of  $C_2H_2$ .  
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## I. INTRODUCTION

Theory has provided information crucial to the resolution of several controversies concerning triplet acetylene. Although Hg-photosensitization experiments by Burton and Hunziker<sup>1</sup> suggested that the lowest triplet state of acetylene would be *trans*-bent, in 1978 Wetmore and Schaefer<sup>2</sup> presented *ab initio* theoretical results reliable enough to show definitively that the *cis*-bent isomer is more stable, at  $T_e \sim 28\,200\text{ cm}^{-1}$  above the ground state. This prediction was confirmed within a year with the observation of the  $^3A_2 \leftarrow ^3B_2$  spectrum by Hunziker and co-workers.<sup>3</sup>

However, subsequent experimental results seemed at odds with these findings. In 1980 Lisy and Klemperer showed experimentally<sup>4</sup> that the lowest Auger detectable metastable triplet state of acetylene must be linear or *trans*-bent since it lacks an electric dipole moment. Moreover, Lundberg and Field (in 1993) presented<sup>5</sup> stimulated emission pumping (SEP) spectra of  $C_2D_2$  which were most easily explained if  $T_0(\textit{cis}^3B_2) \leq 25\,820\text{ cm}^{-1}$ . At that time the singlet–triplet splitting in acetylene was unknown experimentally and the 1978 value was perhaps the most reliable available. In collaboration with Lundberg and Field, Sherrill *et al.*<sup>5</sup> presented more accurate results for the *cis*  $\tilde{a}^3B_2$  and *trans*  $\tilde{a}^3B_u$  states using the coupled-cluster singles, doubles, and perturbative triples method, CCSD(T), in conjunction with a triple- $\zeta$  plus double polarization plus  $f$  functions (TZ2P $f$ ) basis set. The higher-level theoretical treatment actually *increased* the singlet–triplet gap to  $T_0(^3B_2)$

$= 30\,500 \pm 1000\text{ cm}^{-1}$ , with the *trans* isomer about 0.35 eV higher; this definitively ruled out the triplet assignment of the SEP spectra. In this same work, Lundberg and Field explained that there is, in fact, no contradiction between the Lisy and Klemperer experiment<sup>4</sup> and either the Hunziker experiment<sup>3</sup> or the *ab initio* ordering *cis*  $^3B_2$  below *trans*  $^3B_u$ . They argue that any *cis*-bent  $^3B_2$  acetylene formed in the Lisy–Klemperer experiment is rendered Auger undetectable due to electronically allowed spin-orbit mixing with high vibrational levels of the ground electronic state. The Auger detectability of the *trans*  $^3B_u$  state is consistent with the expectation that it experiences much weaker spin-orbit mixing with the ground state, since such mixing is now only *vibronically* allowed.

There have been several subsequent theoretical studies of triplet acetylene. Yamaguchi *et al.*<sup>6</sup> predicted molecular properties of the first four triplet states of acetylene,  $\tilde{a}^3B_2 < \tilde{a}^3B_u < \tilde{b}^3A_u < \tilde{b}^3A_2$ , and additional studies<sup>7,8</sup> have ruled out the possibility that *cis*–*trans* barriers on the  $T_1$  or  $T_2$  surfaces might be responsible for the anomalous sudden increase of detectable Zeeman anticrossings (ZAC) for the  $\tilde{A}^1A_u$  state.<sup>9</sup> Subsequently, Cui, Morokuma, and Stanton<sup>10</sup> found a crossing between the  $S_1$  and  $T_3$  surfaces nearly coincident energetically with the onset of the anomalous ZAC effects, and Cui and Morokuma<sup>11</sup> proposed a nonadiabatic mechanism for the photodissociation of  $S_1$  acetylene involving the first three triplet surfaces. More recent experimental studies by Field and others<sup>12–14</sup> have probed these interac-

tions between triplet states and the  $S_1$  state, and Swiderek *et al.*<sup>15</sup> have observed singlet–triplet transitions in low-energy electron energy loss spectrum of solid acetylene. Malsch *et al.*<sup>16</sup> have presented a detailed analysis of this spectrum together with new theoretical results for vertical excitation energies below about 10 eV and adiabatic excitation energies for the lowest few singlets and triplets using the complete-active-space second-order perturbation theory (CASPT2) method with polarized and augmented triple- $\zeta$  basis sets.

Due to this healthy interplay between theory and experiment in the investigation of triplet states of acetylene, the recent work of Ahmed, Peterka, and Suits<sup>17</sup> is of great interest because it reports for the first time an experimentally derived value for the excitation energy of the lowest triplet state,  $T_0(\tilde{a}^3B_2)$ , of this simplest alkyne. These workers used the velocity map imaging technique to study the 243 nm photodissociation of vinyl radical,  $C_2H_3$ . By conservation of momentum, the major products are shown to be the singlet states of acetylene and vinylidene. However, a minor product is seen with a very low total translational energy release peaking at only 0.23 kcal mol<sup>-1</sup>. Given the current theoretical data, such slow H atoms could only be accounted for by the  $\tilde{a}^3B_2$  state of acetylene. Using the experimental heats of formation of  $C_2H_3$  and  $H(^2S)$ , the authors derive an upper limit for  $T_0(\tilde{a}^3B_2)$  of 82.65 kcal mol<sup>-1</sup>, or 28 900 cm<sup>-1</sup>, which “does not agree well with recent *ab initio* calculations” yielding<sup>5</sup>  $T_0 = 30\,500$  cm<sup>-1</sup>.

In this work, we use state-of-the-art theoretical methods to examine potential sources of error in the earlier *ab initio* adiabatic excitation energies for the four lowest-lying triplet states of acetylene and the three lowest-lying electronic states of vinylidene. By accounting for core-valence correlation, estimating the effects of full (i.e., nonperturbative) inclusion of connected triple excitations, extrapolating to the complete basis set limit, and even estimating relativistic effects, we are able to determine excitation energies for these  $C_2H_2$  species which for the first time may be expected to be of “chemical accuracy,”  $\pm 1$  kcal mol<sup>-1</sup> or better. Our present value for  $T_0(^3B_2) = 30\,900 \pm 230$  cm<sup>-1</sup> demonstrates that recent experimental value of 28 900 cm<sup>-1</sup> is definitely underestimated. Possible reasons for this underestimation have already been suggested by Ahmed *et al.*<sup>17</sup> As those researchers plan to use larger photon energies in future experiments, our results for the higher triplet states should be helpful in interpreting forthcoming experimental data.

## II. THEORETICAL APPROACH

This study employed the correlation-consistent polarized valence basis sets of Dunning and co-workers.<sup>18</sup> Structures and harmonic vibrational frequencies were determined using the correlation-consistent polarized valence triple- $\zeta$  set, denoted cc-pVTZ. The harmonic vibrational frequencies were obtained via finite differences of analytic gradients.<sup>19</sup> Single-point energies were determined using the quadruple- and quintuple- $\zeta$  sets (cc-pVQZ and cc-pV5Z) to enable extrapolations to the basis set limit.<sup>20</sup> The cc-pV5Z basis set for  $C_2H_2$  comprises 292 contracted Gaussian functions and is far larger than in any previous study of triplet states of  $C_2H_2$ .

Additionally, for the first time we have investigated the importance of core correlation in excited states of  $C_2H_2$  via the triple- $\zeta$  core-valence<sup>21</sup> correlation-consistent basis set, denoted cc-pCVTZ.

Electron correlation was accounted for using the reliable coupled-cluster singles and doubles method with a perturbative treatment of connected triple excitations, CCSD(T),<sup>22,19</sup> based on a restricted Hartree–Fock (RHF) reference for the closed-shell singlets and a restricted open-shell Hartree–Fock (ROHF) reference for the triplets. To estimate the error in this method, single-point energies were obtained for the smallest basis, cc-pVTZ, with the complete noniterative treatment of triples, CCSDT.<sup>23,24</sup> Core orbitals (carbon 1s-like) were constrained to be doubly occupied for all correlated computations using the cc-pVXZ basis sets, whereas core electrons were correlated when using the cc-pCVXZ core-valence basis sets. Relativistic effects were considered by a perturbative treatment of the Cowan–Griffin quasi-relativistic many-electron Hamiltonian (which includes the mass-velocity and one-electron Darwin operators) using the CCSD(T) relaxed density.<sup>25</sup> All coupled-cluster computations were performed using the ACES II quantum chemistry program package.<sup>26</sup>

We have also obtained optimized geometries, harmonic vibrational frequencies, and excitation energies using density functional theory<sup>27</sup> (DFT) so that this increasingly popular approach may be compared to our highly accurate coupled-cluster results. Specifically, we used the B3LYP method,<sup>28</sup> which pairs Becke’s hybrid exchange functional<sup>29</sup> with the correlation functional of Lee, Yang, and Parr.<sup>30</sup> The B3LYP computations used unrestricted orbitals for triplet species and were performed with the Q-Chem quantum chemistry package<sup>31</sup> using the cc-pVTZ basis and a grid with 100 radial points and 302 angular points per radial point. Finally, we also report excitation energies using the new Gaussian-3//B3LYP (G3//B3LYP) method<sup>32,33</sup> for thermochemistry, which mixes the results of many *ab initio* computations and adjusts them using a small number of empirical parameters to obtain energy differences which are often accurate to nearly  $\pm 1$  kcal/mol ( $\pm 350$  cm<sup>-1</sup>). The MP4 energies required by the G3//B3LYP procedure, as well as the B3LYP vibrational frequencies for  $\tilde{b}^3A_2$  vinylidene, were provided by J. Rienstra-Kiracofe<sup>34</sup> using the GAUSSIAN 94 program.<sup>35</sup> The reliability of G3//B3LYP for adiabatic excitation energies is assessed by comparison to our best coupled-cluster results.

## III. RESULTS AND DISCUSSION

### A. Structures

Equilibrium geometries, obtained via the B3LYP and CCSD(T) methods with a cc-pVTZ basis set, are given in Table I. The systematic study of several small closed-shell molecules by Thomas *et al.*<sup>36</sup> suggests that the coupled-cluster bond lengths at this level of theory should be accurate within about 0.2%. Compared to experiment,<sup>37</sup> our cc-pVTZ CCSD(T) bond lengths are slightly overestimated (by 0.6% and 0.2%) for ground state acetylene. Larger basis set or an

TABLE I. Theoretical equilibrium geometries for low-lying electronic states of acetylene and vinylidene using the cc-pVTZ basis set.

| State                 | Method                  | $r_e(\text{CC})$<br>(Å) | $r_e(\text{CH})$<br>(Å) | $\theta_e(\text{CCH})$<br>(degrees) |
|-----------------------|-------------------------|-------------------------|-------------------------|-------------------------------------|
| Acetylene             |                         |                         |                         |                                     |
| $\bar{X}^1\Sigma_g^+$ | B3LYP                   | 1.196                   | 1.062                   | 180.0                               |
|                       | CCSD(T)                 | 1.210                   | 1.064                   | 180.0                               |
|                       | Experiment <sup>a</sup> | 1.210                   | 1.064                   | 180.0                               |
| $\bar{a}^3B_2$        | B3LYP                   | 1.324                   | 1.092                   | 128.6                               |
|                       | CCSD(T)                 | 1.340                   | 1.091                   | 128.0                               |
| $\bar{a}^3B_u$        | B3LYP                   | 1.326                   | 1.084                   | 132.2                               |
|                       | CCSD(T)                 | 1.345                   | 1.082                   | 131.5                               |
| $\bar{b}^3A_u$        | B3LYP                   | 1.371                   | 1.094                   | 121.7                               |
|                       | CCSD(T)                 | 1.386                   | 1.094                   | 120.5                               |
| $\bar{b}^3A_2$        | B3LYP                   | 1.346                   | 1.096                   | 130.9                               |
|                       | CCSD(T)                 | 1.360                   | 1.095                   | 130.3                               |
| Vinylidene            |                         |                         |                         |                                     |
| $\bar{X}^1A_1$        | B3LYP                   | 1.291                   | 1.087                   | 120.4                               |
|                       | CCSD(T)                 | 1.307                   | 1.086                   | 120.1                               |
| $\bar{a}^3B_2$        | B3LYP                   | 1.309                   | 1.091                   | 121.2                               |
|                       | CCSD(T)                 | 1.326                   | 1.089                   | 120.8                               |
|                       | Experiment <sup>b</sup> | 1.346 ± 0.040           | 1.090 ± 0.009           | 118.9 ± 2.7                         |
| $\bar{b}^3A_2$        | B3LYP                   | 1.426                   | 1.095                   | 122.7                               |
|                       | CCSD(T)                 | 1.436                   | 1.093                   | 122.4                               |

<sup>a</sup>Experimental results from Baldacci *et al.* (Ref. 37).

<sup>b</sup>Derived from Franck–Condon simulations of experimental spectra by Ervin *et al.* (Ref. 38) based on theoretical parameters for  $\bar{X}^1A_1$  vinylidene.

inclusion of core-valence correlation brought these bond lengths into closer agreement with experiment, but these small geometry changes had essentially no effect on excitation energies. Both the B3LYP and CCSD(T) bond lengths for  $\bar{a}^3B_2$  vinylidene are within the given error bars for the structure derived from Franck–Condon simulations of experimental spectra by Ervin *et al.*<sup>38</sup> The B3LYP and CCSD(T) bond lengths for all states are in fairly good agreement with each other, with very similar C–H bonds and C–C bonds about 0.01 to 0.02 Å shorter for B3LYP. This is consistent with our general experience with these two methods using a cc-pVTZ basis.<sup>39</sup> The CCH bond angle differs by as much as 1.2° ( $\bar{b}^3A_u$  acetylene).

## B. Vibrational frequencies and zero-point energies

Harmonic vibrational frequencies are given in Table II. Compared to the harmonic frequencies derived from experiment<sup>40</sup> for the ground electronic state, the cc-pVTZ CCSD(T) results are within 6 cm<sup>-1</sup> for all modes except the  $\omega_4(\pi_g)$  bend, which differs by 46 cm<sup>-1</sup> (7%); this particular mode is sensitive to basis set effects.<sup>36</sup> B3LYP is more accurate for this mode (reducing the error to 28 cm<sup>-1</sup>) but is worse than CCSD(T) for other modes (the largest error being 62 cm<sup>-1</sup> for  $\omega_2$ ). Overall, the zero-point vibrational energy determined from the CCSD(T) harmonic frequencies, 5785 cm<sup>-1</sup>, is nearly the same as the experimental zero-point energy which may be derived<sup>41</sup> from the harmonic frequencies and anharmonic constants of Strey and Mills,<sup>40</sup> 5755 cm<sup>-1</sup>.

Assuming the other minima considered will generally behave similarly to ground state acetylene, we estimate the zero-point energies simply as one-half of the sum of the the-

oretical harmonic frequencies. Although the CH<sub>2</sub> rocking motion in  $\bar{X}^1A_1$  vinylidene is known to exhibit substantial anharmonicity,<sup>38</sup> Stanton and Gauss have found<sup>42</sup> that anharmonic effects lower the acetylene–vinylidene energy difference by a modest 18 cm<sup>-1</sup>. One might also expect significant anharmonicity for the  $\bar{a}^3B_u$  and  $\bar{b}^3A_2$  states of acetylene, which lie only about 1700 and 1800 cm<sup>-1</sup>, respectively, below the barrier to *cis-trans* isomerization on their respective potential energy surfaces.<sup>43,8</sup> Perhaps more importantly, vibrational frequency predictions for antisymmetric modes of excited electronic states can sometimes be theoretically challenging, and we have encountered such problems for three different vibrational modes: the  $\omega_4$  mode of  $\bar{b}^3A_2$  vinylidene and the  $\omega_6$  modes of  $\bar{b}^3A_u$  and  $\bar{b}^3A_2$  acetylene.

Previous studies<sup>6,8</sup> have shown large variations in the predicted antisymmetric frequencies for the  $T_2$  minima of acetylene,  $^3A_u$  and  $^3A_2$ . Our B3LYP and CCSD(T) results for the  $\omega_4$  and  $\omega_5$  modes of these two structures are in good agreement with each other and with previous equation-of-motion (EOM) CCSD results.<sup>8</sup> For the  $\omega_6$  mode, we observe much larger differences between B3LYP and CCSD(T): 810 versus 934 cm<sup>-1</sup> ( $^3A_u$ ) and 743 versus 863 cm<sup>-1</sup> ( $^3A_2$ ), with even larger differences in the infrared intensities. Previous double- $\zeta$  plus polarization (DZP) EOM-CCSD results for  $\omega_6$  are 710 cm<sup>-1</sup> ( $^3A_u$ ) and 206 cm<sup>-1</sup> ( $^3A_2$ ), while improving the basis set to TZ2P gave 438 cm<sup>-1</sup> ( $^3A_2$ ). The present results for  $\omega_6$  of  $^3A_2$  acetylene seem more plausible than the former EOM-CCSD results, given the reasonable agreement between B3LYP and CCSD(T) and the  $\omega_6$  bending frequency of about 1100 cm<sup>-1</sup> for the  $^3B_2$  state; never-

TABLE II. Theoretical harmonic vibrational frequencies ( $\text{cm}^{-1}$ ), infrared intensities ( $\text{km mol}^{-1}$ ), and zero-point vibrational energies (ZPVE,  $\text{cm}^{-1}$ ) for low-lying electronic states of acetylene and triplet vinylidene using the cc-pVTZ CCSD(T) method.

| State                   | Method                           | $\omega_1$ | $\omega_2$ | $\omega_3$ | $\omega_4$ | $\omega_5$ | $\omega_6$ | ZPVE |
|-------------------------|----------------------------------|------------|------------|------------|------------|------------|------------|------|
| Acetylene               |                                  |            |            |            |            |            |            |      |
| $\tilde{X}^1\Sigma_g^+$ | B3LYP                            | 3516 (0)   | 2070 (0)   | 3412 (89)  | 652 (0)    | 767 (192)  | ...        | 5918 |
|                         | CCSD(T)                          | 3511 (0)   | 2001 (0)   | 3410 (83)  | 578 (0)    | 746 (178)  | ...        | 5785 |
|                         | Experiment <sup>a</sup> $\omega$ | 3495       | 2008       | 3415 (71)  | 624 (0)    | 747 (175)  | ...        |      |
|                         | Experiment <sup>b</sup> $\nu$    | 3374       | 1974       | 3289       | 612        | 730        | ...        |      |
| $\tilde{a}^3B_2$        | B3LYP                            | 3064 (6)   | 1633 (5)   | 821 (2)    | 802 (0)    | 3024 (31)  | 1099 (21)  | 5222 |
|                         | CCSD(T)                          | 3109 (3)   | 1578 (3)   | 817 (1)    | 767 (0)    | 3076 (19)  | 1104 (18)  | 5226 |
| $\tilde{a}^3B_u$        | B3LYP                            | 3153 (0)   | 1612 (0)   | 1080 (0)   | 898 (75)   | 3134 (13)  | 744 (36)   | 5311 |
|                         | CCSD(T)                          | 3199 (0)   | 1542 (0)   | 1080 (0)   | 868 (62)   | 3184 (7)   | 758 (32)   | 5316 |
| $\tilde{b}^3A_u$        | B3LYP                            | 3049 (0)   | 1422 (0)   | 1110 (0)   | 845 (5)    | 3039 (37)  | 810 (268)  | 5138 |
|                         | CCSD(T)                          | 3079 (0)   | 1385 (0)   | 1126 (0)   | 850 (7)    | 3071 (31)  | 934 (65)   | 5223 |
| $\tilde{b}^3A_2$        | B3LYP                            | 3013 (13)  | 1535 (3)   | 820 (19)   | 1036 (0)   | 2967 (47)  | 743 (344)  | 5057 |
|                         | CCSD(T)                          | 3057 (7)   | 1493 (1)   | 824 (16)   | 1033 (0)   | 3016 (51)  | 863 (181)  | 5143 |
| Vinylidene              |                                  |            |            |            |            |            |            |      |
| $\tilde{X}^1A_1$        | B3LYP                            | 3111 (46)  | 1712 (88)  | 1217 (25)  | 757 (77)   | 3187 (19)  | 345 (7)    | 5165 |
|                         | CCSD(T)                          | 3130 (38)  | 1662 (82)  | 1227 (17)  | 746 (76)   | 3221 (15)  | 339 (9)    | 5163 |
| $\tilde{a}^3B_2$        | B3LYP                            | 3017 (5)   | 1583 (6)   | 1399 (2)   | 752 (1)    | 3083 (5)   | 992 (3)    | 5413 |
|                         | CCSD(T)                          | 3061 (4)   | 1545 (5)   | 1409 (3)   | 762 (9)    | 3142 (4)   | 1002 (2)   | 5461 |
|                         | Experiment <sup>c</sup> $\nu$    | 2930       | 1530       | 1375       |            |            |            |      |
| $\tilde{b}^3A_2$        | B3LYP                            | 2992 (18)  | 1455 (6)   | 1191 (13)  | 1236 (236) | 3058 (19)  | 895 (5)    | 5413 |
|                         | CCSD(T)                          | 3035 (8)   | 1471 (8)   | 1191 (20)  | 882 (<1)   | 3117 (12)  | 904 (6)    | 5300 |

<sup>a</sup>Experimental harmonic frequencies from Strey and Mill (Ref. 40) for frequencies and from Koops *et al.* (Ref. 56) for intensities.

<sup>b</sup>Experimental fundamental frequencies tabulated by Shimanouchi (Ref. 57).

<sup>c</sup>Experimental fundamental frequencies of Ervin *et al.* (Ref. 38).

theless, the current predictions for this vibrational frequency must be treated with caution.

Similar difficulties arise for the  $\tilde{b}^3A_2$  state of vinylidene, where  $\omega_4$  out-of-plane ( $b_1$ ) vibrational mode allows coupling to the lower-lying  $\tilde{a}^3B_2$  state. Here we obtain  $1236 \text{ cm}^{-1}$  for B3LYP versus  $882 \text{ cm}^{-1}$  for CCSD(T). The former value is fortuitously identical to that obtained at the TZ2P EOM-CCSD level of theory.<sup>44</sup> Again, the discrepancies indicate that the predictions for this frequency are not as reliable as one would expect for this level of theory.

In an effort to understand the difficulty in obtaining consistent theoretical predictions for these problematic vibrational modes, we obtained the eigenvalues of the molecular orbital (MO) Hessian (spin-preserving rotations only)<sup>45</sup> for each structure at the cc-pVTZ CCSD(T) optimized geometry. Burton *et al.* suggested that negative eigenvalues of the MO Hessian could lead to anomalous Hartree–Fock vibrational frequencies,<sup>46</sup> and more recently Crawford *et al.*<sup>47</sup> have shown how near-zero MO Hessian eigenvalues can cause spurious vibrational frequencies not only for Hartree–Fock but also for correlated wave functions based on a Hartree–Fock reference. Two negative eigenvalues each were found for the  $^3A_u$  and  $^3A_2$  states of acetylene, but none were found for  $^3A_2$  vinylidene, which exhibits the worst vibrational frequency discrepancy. Concerning near-zero eigenvalues, only two eigenvalues less than 0.01 were found:  $-0.009$  ( $^3A_u$ ) and  $0.005$  ( $^3B_u$ ). While the  $^3A_u$  state was problematic, the  $^3B_u$  state was not; moreover, all eigenvalues for the difficult  $^3A_2$  state of vinylidene were greater than 0.03, whereas several eigenvalues smaller than this caused no problems for other states. Hence, it does not seem possible in this case to find an easy link between negative or

near-zero MO Hessian eigenvalues and all three difficult vibrational modes, and it is unclear whether the situation could be improved by using a different choice of orbitals (e.g., approximate Brueckner orbitals<sup>48,49</sup>). For  $^3A_2$  vinylidene, the problem may simply be that the  $\omega_4(b_1)$  vibrational mode lowers the symmetry to  $C_s$ , where mixing can occur with the nearby  $^3B_2$  state. This is not the case for the two minima on the  $T_2$  surface of acetylene, where the problematic  $\omega_6$  vibrational mode does not allow coupling to the  $T_1$  minima.

The difficult vibrational modes have a considerably larger uncertainty than the others. The ZPVEs, computed as one-half the sum of the cc-pVTZ CCSD(T) harmonic vibrational frequencies, should be accurate to roughly  $\pm 150 \text{ cm}^{-1}$  for the well-behaved states. For  $\tilde{b}^3A_u$  and  $\tilde{b}^3A_2$  acetylene, we will use a somewhat higher uncertainty of  $\pm 200 \text{ cm}^{-1}$ , and for the challenging  $\tilde{b}^3A_2$  state of vinylidene, we will estimate an uncertainty of perhaps  $\pm 300 \text{ cm}^{-1}$ .

### C. Adiabatic excitation energies

The total energies are given in Table III, and from these we determine the relative energies presented in Table IV. In this study, the baseline excitation energies are obtained at the cc-pVTZ CCSD(T) level of theory, which was used to obtain geometries and harmonic vibrational frequencies; corrections are obtained by more complete single-point computations at the cc-pVTZ CCSD(T) optimized geometries. First we will describe our procedure for obtaining highly accurate equilibrium excitation energies,  $T_e$ , and then we will add the zero-point vibrational energy (ZPVE) corrections to obtain  $T_0$  values which may be compared to experiment. For the lowest triplet state,  $\tilde{a}^3B_2$  cis, our baseline result of  $T_e$

TABLE III. Total energies (hartrees, subtract 77) and energy corrections (hartrees) for low-lying electronic states of acetylene and triplet states of vinylidene, evaluated at cc-pVTZ CCSD(T) geometries except where otherwise noted.

|  | Acetylene             |                |                |                |                | Vinylidene     |                |                |
|--|-----------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
|  | $\bar{X}^1\Sigma_g^+$ | $\bar{a}^3B_2$ | $\bar{a}^3B_u$ | $\bar{b}^3A_u$ | $\bar{b}^3A_2$ | $\bar{X}^1A_1$ | $\bar{a}^3B_2$ | $\bar{b}^3A_2$ |
| QZ(3df,3pd) CCSD(T)//CISD <sup>a</sup> | -0.196 919            | -0.056 627     | -0.043 862     | -0.033 682     | -0.021 871     |                |                |                |
| cc-pVTZ B3LYP//B3LYP                   | -0.312 387            | -0.174 339     | -0.160 326     | -0.155 127     | -0.145 406     | -0.243 104     | -0.167 942     | -0.152 045     |
| cc-pVTZ CCSD(T)                        | -0.187 648            | -0.047 011     | -0.034 104     | -0.023 454     | -0.011 790     | -0.117 042     | -0.044 749     | -0.021 439     |
| cc-pVTZ CCSDT                          | -0.187 691            | -0.048 493     | -0.036 834     | -0.024 681     | -0.013 121     | -0.117 834     | -0.045 677     | -0.022 523     |
| cc-pCVTZ CCSD(T)                       | -0.289 797            | -0.147 975     | -0.135 083     | -0.124 090     | -0.112 618     | -0.218 348     | -0.145 847     | -0.121 976     |
| cc-pVQZ CCSD(T)                        | -0.209 297            | -0.066 773     | -0.053 840     | -0.043 536     | -0.032 184     | -0.137 803     | -0.064 196     | -0.040 897     |
| cc-pV5Z CCSD(T)                        | -0.215 745            | -0.072 697     | -0.059 792     | -0.049 668     | -0.038 346     | -0.144 071     | -0.069 980     | -0.046 779     |
| CBS CCSD(T)                            | -0.221 337            | -0.077 711     | -0.064 775     | -0.054 810     | -0.043 543     | -0.149 424     | -0.074 878     | -0.051 720     |
| Core-valence correction                | -0.102 149            | -0.100 964     | -0.100 979     | -0.100 636     | -0.100 828     | -0.101 306     | -0.101 098     | -0.100 537     |
| Full T correction                      | -0.000 043            | -0.001 482     | -0.002 730     | -0.001 227     | -0.001 331     | -0.000 792     | -0.000 928     | -0.001 084     |
| Relativistic correction                | -0.029 754            | -0.029 768     | -0.029 721     | -0.029 842     | -0.029 795     | -0.029 888     | -0.029 726     | -0.029 878     |
| Corrected CBS CCSD(T)                  | -0.353 283            | -0.209 925     | -0.198 205     | -0.186 515     | -0.175 497     | -0.281 410     | -0.206 630     | -0.183 219     |
| G3//B3LYP                              | -0.292 367            | -0.151 931     | -0.139 257     | -0.128 040     | -0.116 849     | -0.222 944     | -0.147 738     | -0.124 011     |

<sup>a</sup>Results from Yamaguchi *et al.* (Ref. 6).

=30 870 cm<sup>-1</sup> is only slightly lower than the previous TZ2P *f* CCSD(T)//DZP CISD value of  $T_e = 31\,000$  cm<sup>-1</sup>; this indicates a fairly small effect due to refinement of the geometry and the differences in basis set (cc-pVTZ differs from TZ2P *f* primarily in the addition of *d* functions on hydrogens).

As suggested previously,<sup>5</sup> we find that larger basis sets (here, cc-pVQZ and cc-pV5Z) increase the excitation energy of the lowest triplet state; moreover, the excitation energies of the vinylidene states and the other triplet states of acetylene are also increased. If we hope to achieve chemical accuracy,  $\pm 1$  kcal mol<sup>-1</sup> ( $\pm 350$  cm<sup>-1</sup>), then we must consider these basis set effects to be quite large: the quadruple- $\zeta$  basis set increases excitation energies by  $\sim 200$ – $500$  cm<sup>-1</sup>, while the quintuple- $\zeta$  basis increases them by an additional  $\sim 100$

cm<sup>-1</sup>. Based on the recommendations of Halkier *et al.*,<sup>20</sup> we may extrapolate the correlation energy to the complete basis set limit by fitting cc-pVQZ and cc-pV5Z CCSD(T) correlation energies to the form  $E_X^{\text{corr}} = E_\infty^{\text{corr}} + AX^{-3}$ , where  $X$  is the cardinal number of the basis set (4 or 5). This extrapolated correlation energy is then added to the cc-pV5Z Hartree-Fock energy to obtain the estimated complete-basis set (CBS) CCSD(T) energy. The CBS estimates increase the excitation energies yet again by 50–100 cm<sup>-1</sup>, to yield CBS CCSD(T) excitation energies ( $T_e$ ) of 31 520 ( $\bar{a}^3B_2$ ), 34 360 ( $\bar{a}^3B_u$ ), 36 550 ( $\bar{b}^3A_u$ ), and 39 020 cm<sup>-1</sup> ( $\bar{b}^3A_2$ ) for acetylene and 15 780 ( $\bar{X}^1A_1$ ), 32 140 ( $\bar{a}^3B_2$ ), and 37 230 cm<sup>-1</sup> ( $\bar{b}^3A_2$ ) for vinylidene. These values are roughly 600 to 800 cm<sup>-1</sup> (2 kcal mol<sup>-1</sup>) higher than the previous largest basis

TABLE IV. Adiabatic excitation energies  $T_e$  (cm<sup>-1</sup>,  $T_0$  in parentheses) for low-lying triplet states of acetylene.

|  | Acetylene          |                    |                    |                    | Vinylidene         |                    |                    |
|--|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
|  | $\bar{a}^3B_2$     | $\bar{a}^3B_u$     | $\bar{b}^3A_u$     | $\bar{b}^3A_2$     | $\bar{X}^1A_1$     | $\bar{a}^3B_2$     | $\bar{b}^3A_2$     |
| TZ2P <i>f</i> CCSD(T)//DZP CISD <sup>a</sup> | 31 000<br>(30 500) |                    |                    |                    |                    |                    |                    |
| QZ(3df,3pd) CCSD(T)//CISD <sup>b</sup>       | 30 790             | 33 590             | 35 830             | 38 420             |                    |                    |                    |
| TZ(2df,2pd) CASPT2//CASSCF <sup>c</sup>      | 30 200             | 32 600             | 35 600             | 37 900             |                    |                    |                    |
| cc-pVTZ B3LYP                                | 30 300<br>(29 600) | 33 370<br>(32 770) | 34 520<br>(33 740) | 36 650<br>(35 870) | 15 210<br>(14 460) | 31 700<br>(31 200) | 35 190<br>(34 690) |
| cc-pVTZ CCSD(T)                              | 30 870             | 33 700             | 36 040             | 38 600             | 15 500             | 31 360             | 36 480             |
| cc-pVTZ CCSDT                                | 30 550             | 33 110             | 35 780             | 38 310             | 15 330             | 31 170             | 36 250             |
| cc-pCVTZ CCSD(T)                             | 31 130             | 33 960             | 36 370             | 38 890             | 15 680             | 31 590             | 36 830             |
| cc-pVQZ CCSD(T)                              | 31 280             | 34 120             | 36 380             | 38 870             | 15 690             | 31 850             | 36 960             |
| cc-pV5Z CCSD(T)                              | 31 400             | 34 230             | 36 450             | 38 940             | 15 730             | 31 990             | 37 080             |
| CBS CCSD(T)                                  | 31 520             | 34 360             | 36 550             | 39 020             | 15 780             | 32 140             | 37 230             |
| Core correlation correction                  | 260                | 257                | 332                | 290                | 185                | 231                | 354                |
| CCSDT correction                             | -316               | -590               | -260               | -283               | -164               | -194               | -228               |
| Relativistic correction                      | -3                 | 7                  | -19                | -9                 | -29                | 6                  | -27                |
| Final estimate $T_e$                         | 31 460             | 34 040             | 36 600             | 39 020             | 15 770             | 32 190             | 37 330             |
| cc-pVTZ CCSD(T) ZPVE                         | -560               | -470               | -560               | -640               | -620               | -320               | -490               |
| Final estimate $T_0$                         | (30 900)           | (33 570)           | (36 040)           | (38 380)           | (15 150)           | (31 870)           | (36 840)           |
| G3//B3LYP                                    | (30 820)           | (33 600)           | (36 070)           | (38 520)           | (15 240)           | (31 740)           | (36 950)           |

<sup>a</sup>Results from Lundberg *et al.* (Ref. 5).<sup>b</sup>Results from Yamaguchi *et al.* (Ref. 6).<sup>c</sup>Results from Malsch *et al.* (Ref. 16).

set results of Yamaguchi *et al.*<sup>6</sup> for triplet acetylene. Exploratory computations adding diffuse *s*- and *p*-type functions to the cc-pV5Z basis confirmed the expectation that these valence excited states do not have any appreciable neglected diffuse character, and so we estimate the uncertainty in the CBS extrapolations as  $\pm 100$  cm<sup>-1</sup>.

One would expect the largest errors in the CBS CCSD(T) results to come from the neglect of core correlation and the incomplete (perturbative) treatment of connected triple excitations in the CCSD(T) method; the neglect of connected quadruple and higher-order excitations is another, presumably much smaller, source of error. The effect of core correlation was estimated by correlating all electrons in CCSD(T) with the cc-pCVTZ basis set, which adds basis functions describing core correlation to the cc-pVTZ basis. As seen in Table IV, core correlation is significant and roughly uniform across the triplets, increasing excitation energies by 230 to 350 cm<sup>-1</sup>. By comparison, core correlation increases<sup>21</sup> the singlet–triplet gap in CH<sub>2</sub> by about 150 cm<sup>-1</sup> (although in CH<sub>2</sub>, singlet and triplet states are reversed). For  $\bar{a}^3B_2$  acetylene, we verified that this core correlation correction (260 cm<sup>-1</sup>) is not changed substantially for a larger cc-pCVQZ basis (242 cm<sup>-1</sup>). We estimate the uncertainty in the core correlation correction as double this difference, or  $\pm 36$  cm<sup>-1</sup>.

Errors in the treatment of electron correlation were estimated in the cc-pVTZ basis by including the full, iterative treatment of triples via the CCSDT method. The correction is negative and less uniform than the core correlation correction, decreasing excitation energies by 160 to 590 cm<sup>-1</sup>. CCSDT computations for  $\bar{a}^3B_2$  acetylene verify that this full triples correction is hardly affected ( $-2$  cm<sup>-1</sup>) by improving the basis set to cc-pVQZ. In a TZ2P basis, this correction is 70 cm<sup>-1</sup> for the methylene singlet–triplet gap, and benchmark full configuration interaction results<sup>50</sup> indicate that the remaining error due to neglect of quadruple and higher-order excitations is about 30 cm<sup>-1</sup>; thus it seems safe to estimate the uncertainty in the correlation treatment for C<sub>2</sub>H<sub>2</sub> as  $\pm 100$  cm<sup>-1</sup>.

Additional sources of error in the equilibrium excitation energies,  $T_e$ , should be substantially smaller than those already estimated. These include remaining deficiencies in the basis set and correlation treatment (discussed above), relativistic effects, and errors in the Born–Oppenheimer approximation. Relativistic effects may be estimated via a perturbative treatment of the mass-velocity and one-electron Darwin terms using the relaxed CCSD(T) density; not surprisingly, we find that they have very little effect on the excitation energies—the largest change is a lowering of  $\bar{X}^1A_1$  vinylidene by 29 cm<sup>-1</sup>, and we estimate uncertainties due to relativistic effects as half this, or  $\pm 15$  cm<sup>-1</sup>. A potentially larger relativistic effect could be due to spin-orbit coupling. However, a quick estimate by Pederson<sup>51</sup> using a density functional theory (DFT) approach<sup>52</sup> indicates that spin-orbit effects are negligible in acetylene. We have not explicitly considered corrections to the Born–Oppenheimer approximation, but we note that the Born–Oppenheimer diagonal correction to the singlet–triplet gap<sup>53</sup> is 40 cm<sup>-1</sup> for CH<sub>2</sub> and 28 cm<sup>-1</sup> for HCF. We postulate that the Born–Oppenheimer

correction to the singlet–triplet gap in C<sub>2</sub>H<sub>2</sub> is probably not more than twice this ( $\pm 80$  cm<sup>-1</sup>).

To obtain our final estimates of the excitation energies  $T_e$ , we add the core correlation correction, the relativistic correction, and the full CCSDT correction (all obtained with the cc-pVTZ or cc-pCVTZ basis sets) to the CBS CCSD(T) results. Our best estimates of  $T_e$  for acetylene are 31 460 ( $\bar{a}^3B_2$ ), 34 040 ( $\bar{a}^3B_u$ ), 36 600 ( $\bar{b}^3A_u$ ), and 39 020 cm<sup>-1</sup> ( $\bar{b}^3A_2$ ), and for vinylidene they are 15 770 ( $\bar{X}^1A_1$ ), 32 190 ( $\bar{a}^3B_2$ ), 37 330 cm<sup>-1</sup> ( $\bar{b}^3A_2$ ). Combining the uncertainties given above, we obtain an overall uncertainty in these term energies of about  $\pm 170$  cm<sup>-1</sup>.

To compare to experiment, we must add the zero-point vibrational energy (ZPVE) corrections to obtain  $T_0$  from  $T_e$ . Using the cc-pVTZ CCSD(T) ZPVEs, we obtain best estimates for  $T_0$  of 30 900  $\pm$  230 ( $\bar{a}^3B_2$ ), 33 570  $\pm$  230 ( $\bar{a}^3B_u$ ), 36 040  $\pm$  260 ( $\bar{b}^3A_u$ ), and 38 380  $\pm$  260 ( $\bar{b}^3A_2$ ) cm<sup>-1</sup> for acetylene and 15 150  $\pm$  230 ( $\bar{X}^1A_1$ ), 31 870  $\pm$  230 ( $\bar{a}^3B_2$ ), and 36 840  $\pm$  350 cm<sup>-1</sup> ( $\bar{b}^3A_2$ ) for vinylidene. Our result for the acetylene–vinylidene energy difference (15 150 cm<sup>-1</sup>) is in excellent agreement with the recent estimate of 15 199  $\pm$  205 cm<sup>-1</sup> by Stanton and Gauss<sup>42</sup> using similar complete-basis-set extrapolations of coupled-cluster energies. The present data show that the previous<sup>5</sup> TZ2Pf CCSD(T) excitation energy for the first triplet state of acetylene,  $T_0(\bar{a}^3B_2) = 30 500 \pm 1000$  cm<sup>-1</sup>, is correct within its estimated error bounds and the recent experimentally derived estimate<sup>17</sup>  $T_0 = 28 900$  cm<sup>-1</sup> is definitely too low. A possible explanation for this discrepancy has already been given by Ahmed, Peterka, and Suits, who point out that their observation of triplet acetylene below the *ab initio* threshold could be caused by “hot band” contributions from vibrationally excited vinyl radicals. We note that the uncertainty in the heat of formation of vinyl radical,<sup>54</sup>  $\pm 5$  kJ mol<sup>-1</sup> (420 cm<sup>-1</sup>), is not nearly large enough to explain the discrepancy with experiment, and the uncertainty in the heat of formation of H atom is nearly negligible. Suits and co-workers are planning future experiments with larger photon energies which may access the higher-lying triplet states. We anticipate that the accurate excitation energies reported here for the other states of acetylene and vinylidene will assist in the interpretation of these experiments.

#### D. Comparison of electronic structure methods

Finally, we now consider the ability of some other *ab initio* approaches to match our benchmark complete-basis-set coupled-cluster estimates. Table IV shows that the TZ(2df,2pd) CASPT2//CASSCF results of Malsch *et al.*<sup>16</sup> for  $T_e$  are about 1000 to 1400 cm<sup>-1</sup> too low for the four acetylene excited states. The primary causes of this underestimation are both basis set and correlation effects. DFT B3LYP excitation energies ( $T_0$ ) are also uniformly underestimated, by 700 to 2500 cm<sup>-1</sup> (2 to 7 kcal mol<sup>-1</sup>). Clearly this approach is not suitable for obtaining excitation energies within chemical accuracy. On the other hand, the recently introduced G3 method,<sup>32</sup> which generally provides heats of formation to near-chemical accuracy, fares much better for the current problem.

The G3 method combines results from a series of *ab initio* computations to mimic—at reduced computational expense—the results of a large basis set quadratic configuration interaction singles and doubles with perturbative triples [QCISD(T)]<sup>55</sup> treatment. This approach includes an estimate of core correlation and an empirical adjustment for remaining deficiencies in the treatment of electron correlation, so that in principle it is capable of providing high-quality relative energies comparable to the present complete basis coupled-cluster results. Although G3 has been benchmarked against a large number of experimental heats of formation, ionization potentials, and electron affinities,<sup>32</sup> it is important to evaluate its performance for adiabatic excitation energies. Here we have employed the G3//B3LYP variant,<sup>33</sup> which uses B3LYP for geometries and frequencies. Table IV shows that our G3//B3LYP excitation energies are a dramatic improvement over the cc-pVTZ B3LYP energies, differing from our final coupled-cluster estimates by only 30–140 cm<sup>-1</sup> (0.1–0.4 kcal mol<sup>-1</sup>), which is less than our estimated uncertainties. Given that cc-pV5Z CCSD(T) was vastly more expensive than any of the computations required for G3//B3LYP, this suggests that G3//B3LYP may be the method of choice for routine computations of adiabatic excitation energies of “well-behaved” molecules. One would expect G3//B3LYP to make larger errors for systems exhibiting significant nondynamical correlation (e.g., highly strained species or molecules undergoing bond-breaking reactions) and for systems containing heavier atoms where relativistic effects can become important.

#### IV. CONCLUSIONS

The singlet–triplet gap in acetylene and the identity of the first excited triplet state have been controversial questions that theory claims to have answered. However, the first experimentally derived estimate of the singlet–triplet gap recently reported by Ahmed, Peterka, and Suits,<sup>17</sup>  $T_0(\tilde{a}^3B_2) = 28\,900\text{ cm}^{-1}$ , is not in good agreement with the TZ(2*df*,2*p*) CCSD(T)//DZP CISD prediction<sup>5</sup> of  $30\,500 \pm 1000\text{ cm}^{-1}$ . In this study we have investigated possible deficiencies in the previous theoretical treatment of this important energetic quantity. Extrapolating to the complete basis set limit increases the excitation energy by about 650 cm<sup>-1</sup> compared to a triple- $\zeta$  basis, and core correlation adds another 260 cm<sup>-1</sup>. However, these corrections are partially offset by a -316 cm<sup>-1</sup> correction for deficiencies in the CCSD(T) treatment of electron correlation. As expected, relativistic corrections appear to be very small. Our final estimate of  $T_0(\tilde{a}^3B_2) = 30\,900 \pm 230\text{ cm}^{-1}$  is in good agreement with the previous theoretical value and demonstrates that the experimental result is underestimated; the possibility of “hot band” contributions from internally excited vinyl radicals noted by Ahmed *et al.* now seems considerably more likely. To assist future experimental work, we have used the same theoretical methodology to predict term energies for the next three triplet minima of acetylene and the first three states of vinylidene. Finally, we have used our high-quality results to benchmark B3LYP density-functional theory and the G3//B3LYP methods for adiabatic excitation energies, and we find that while G3//B3LYP is within 0.4

kcal mol<sup>-1</sup> of our best results, cc-pVTZ B3LYP is off by as much as 7 kcal mol<sup>-1</sup> and is thus unsuitable for computing highly accurate excitation energies.

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