

# Equilibrium structure and fundamental frequencies of allene†

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The  $r_e$  structure of allene is revised on the basis of high-level quantum chemical calculations (CCSD(T)/cc-pVQZ and CCSD(T)/cc-pCVQZ) as well as *via* analysis of experimental rotational constants for  $C_3H_4$ ,  $C_3D_4$  and  $H_2C_3D_2$  employing vibrational corrections obtained from quantum chemical calculations (SDQ-MBPT(4)/cc-pVTZ). For the equilibrium geometry a least-squares fit to the corrected rotational constants yields  $r(C-H) = 1.081 \text{ \AA}$ ,  $r(C-C) = 1.307 \text{ \AA}$ ,  $\alpha(HCH) = 118.35^\circ$  in satisfactory agreement with a previous, though less precise  $r_e$  structure based on gas-phase electron diffraction data. In addition, computed harmonic and fundamental frequencies are reported and compared to experimental values.

## I. Introduction

Knowledge of molecular structure is an important prerequisite for an understanding of the electronic structure and chemical reactivity of molecules. It is thus not surprising that a lot of effort has been and is devoted to the accurate determination of molecular geometries. Consequently, a large amount of structural information has been obtained during the last decades using a broad selection of experimental techniques ranging from spectroscopy to diffraction methods.<sup>1–6</sup> However, the geometrical parameters usually depend on the technique chosen for their determination and, in most cases, also involve some kind of vibrational averaging. Typically,  $r_0$  and  $r_s$  geometries are obtained from microwave and rotationally resolved infrared investigations by analyzing experimental rotational constants without explicit consideration of vibrational effects. From electron diffraction, vibrationally averaged distances ( $r_g$ ) as well as vibrationally averaged geometries ( $r_z$ ) can be obtained. X-ray structures that are most common in chemistry are probably best characterized as  $r_x$  structures, *i.e.*, vibrationally averaged structures for finite temperatures. For an excellent summary of the definitions of the various structural parameters, the interested reader is referred to ref. 7.

While a direct comparison of geometrical parameters obtained with different experimental techniques is already difficult, it should be also noted that vibrationally averaged structures such as  $r_0$ ,  $r_s$ ,  $r_z$ ,  $r_g$ , *etc.* depend on the isotopomers chosen for the experimental study. Furthermore, these experimental structures are not directly comparable with results from quantum chemical calculations which have evolved to one of the major sources for structural information in chemistry during the last decades.<sup>8</sup> Quantum chemical calculations usually provide so-called  $r_e$  geometries, *i.e.*, geometries which correspond to minima on the Born–Oppenheimer potential energy surface.  $r_e$  geometries can also be determined on the basis of experimental data, but except for diatomic molecules the required procedure is rather tedious.<sup>7</sup> In particular, the additional quantities needed to correct the experimental data (*e.g.*, rotational constants) for vibrational effects are generally not easily accessible. However,  $r_e$  geometries have several advantages and are generally considered the preferred choice. They have a rigorous definition, they are independent of the chosen isotopomer(s),<sup>9</sup> and they are the only geometries which

rigorously exclude vibrational effects and, thus, solely reflect the influence of the electronic structure on the geometry.

Considering these difficulties in the experimental determination of  $r_e$  structures, it is not surprising that accurate  $r_e$  structures have been reported for only a few standard organic molecules.<sup>7</sup> However, a change can be expected here, as it is becoming more and more routine to supply the information about vibrational corrections by means of quantum chemical calculations.<sup>10–13</sup> In particular, the combination of precisely measured rotational constants with computed vibrational corrections has recently gained popularity. This combined use of theory and experiment enabled the accurate determination of a number of equilibrium structures including those for methane,<sup>10,14</sup> ethylene,<sup>15</sup> cyclopropane<sup>16</sup> and benzene.<sup>17</sup>

In this work, we focus on another interesting prototype organic molecule, namely allene. While there is no question concerning its qualitative structural features, the purpose of this work is the determination of a highly accurate equilibrium structure ( $r_e$  structure) for allene. Though  $r_0$  and  $r_z$  structures were reported long ago by Maki and Toth<sup>18</sup> based on experimental rotational constants for  $C_3H_4$  and  $C_3D_4$ , no  $r_e$  structure has been derived from the available rotational constants. More accurate rotational constants of the isotopomers of allene have been reported recently by Hegelund and co-workers.<sup>19–22</sup> These are the values which we use in the combined experimental/theoretical approach to determine the  $r_e$  geometry of allene that is pursued in the present work. However, a  $r_e$  geometry for allene has been reported by Kuchitsu *et al.* in 1987 based on electron diffraction data<sup>23</sup> using a simple, but efficient model to account for vibrational effects on bond distances. According to previous experience,<sup>16</sup>  $r_e$  parameters derived in a such manner are quite reliable, although the error bars are typically larger than for geometrical parameters derived from rotational constants.

In the following, we will:

1. Derive an accurate  $r_e$  structure (with reduced error bars compared to the available  $r_e$  structure) on the basis of measured rotational constants and computed vibrational corrections.
2. Compare the  $r_e$  geometries derived from rotational spectroscopy and electron diffraction with corresponding results from state-of-the-art calculations employing coupled-cluster techniques together with large basis sets.
3. Calculate vibrational corrections to distances, thus enabling a direct comparison of the computational results with experimental  $r_g$  and  $r_z$  structures.

† Dedicated to Professor M. Baudler (Universität zu Köln) on the occasion of her 80th birthday.

4. Compute harmonic and fundamental frequencies for allene and compare them with available experimental gas-phase information from ref. 19.

## II. Computational details

### A. Equilibrium geometries

A large number of computational investigations has shown that the coupled-cluster singles and doubles (CCSD) approach<sup>24</sup> augmented by a perturbative treatment of triple excitations (CCSD(T))<sup>25</sup> yields near-quantitative accuracy provided sufficiently large basis sets are used.<sup>26–29</sup> It has been demonstrated that combination of the CCSD(T) approach with Dunning's cc-pVQZ<sup>30</sup> or preferably cc-pCVQZ set<sup>31</sup> typically provides geometries with a residual error of less than 0.003 Å for bond distances and a few tenths of a degree for bond angles.<sup>15,32,33</sup> On the basis of this experience, geometry optimizations at both the CCSD(T)/cc-pVQZ (285 basis functions) and the CCSD(T)/cc-pCVQZ level (372 basis functions) have been carried out in this work.

However, due to the large number of basis functions the geometry optimizations at the CCSD(T) level had to be carried out using numerically evaluated gradients, as our analytic gradient code<sup>34,35</sup> was not applicable due to disk space bottlenecks.

All geometry optimizations were converged such that the numerical precision of the computed distances is better than 0.0001 Å.

### B. Vibrational corrections to rotational constants

The vibrational dependence of the rotational constants of a molecule can be expressed as

$$B_v = B_e - \sum_r \alpha_r^B(v_r + \frac{1}{2}) + \sum_{r \geq s} \gamma_{rs}^B(v_r + \frac{1}{2})(v_s + \frac{1}{2}) + \dots \quad (1)$$

with  $B_e$  as the corresponding equilibrium value (*i.e.*, the rotational constants for the molecule at the minimum of the Born–Oppenheimer potential energy surface) and  $B_v$  the rotational constant for the vibrational state  $v$ . The sums in eqn. (1) run over normal coordinates  $r$  and  $s$ , while  $\alpha_r^B$  and  $\gamma_{rs}^B$  are the corresponding first- and second-order vibration–rotation interaction constants, respectively. As the contributions due to  $\gamma_{rs}^B$  to  $B_v$  are typically two orders of magnitude smaller, it is justified to consider in the following only the linear correction term which involves  $\alpha_r^B$  (for a detailed discussion see ref. 36). The first-order vibration–rotation interaction constants needed in this context can in principle be obtained from the analysis of rotationally resolved vibrational spectra. However, such an analysis is often complicated, as the complete set of  $\alpha_r^B$  is needed and as the analysis is often hampered by so-called Coriolis resonances. For a compound such as allene, for example, no complete set of  $\alpha_r^B$  is available.

The quantum chemical calculation of  $\alpha_r^B$  thus represents a convenient and attractive alternative which has been successfully used in a number of studies.<sup>10–12,16,17,37,38</sup> A computationally tractable expression for  $\alpha_r^B$  can be derived by perturbation theory starting with a rigid-rotator harmonic-oscillator Hamiltonian. In second order, one obtains<sup>36,39</sup>

$$\alpha_r^B = -\frac{2B_e^2}{\omega_r} \left[ \sum_{\xi} \frac{3(a_r^{(b\xi)})^2}{4I_{\xi}} + \sum_s (\zeta_{r,s}^{(b)})^2 \frac{(3\omega_r^2 + \omega_s^2)}{\omega_r^2 - \omega_s^2} + \pi \left( \frac{c}{h} \right)^{1/2} \sum_s \phi_{rrs} a_s^{(bb)} \left( \frac{\omega_r}{\omega_s^{3/2}} \right) \right] \quad (2)$$

with  $\omega_r$  as the harmonic frequency of the  $r$ th mode,  $I_{\xi}$  the  $\xi$ th principal components of the inertia tensor at the equilibrium geometry and  $a_r^{(ab)}$  the corresponding derivative of  $I_{ab}$  with respect to the normal coordinate  $Q_r$ . Furthermore,  $\zeta_{r,s}^{(b)}$  denotes the Coriolis matrices and  $\phi_{rst}$  the cubic force con-

stants defined in terms of the dimensionless normal coordinates  $q_r$  (see ref. 36 for definitions and the derivation of eqn. (2)).

While all three terms in eqn. (2) are of similar importance it should be noted that the first two terms just require knowledge of the harmonic force field and thus are computationally inexpensive. The third term requires evaluation of the cubic force field, *i.e.*, the third derivatives of the energy with respect to  $q_r$ , and thus represents the computational bottleneck in the calculation of  $\alpha_r^B$ . It is also the only term which includes anharmonic effects of the rectilinear force field.

To reduce computational cost, we computed the quadratic and cubic force field needed for the calculation of the vibration–rotation interaction constants at the SDQ-MBPT(4) (*i.e.*, fourth-order many-body-perturbation theory without contributions due to triple excitations)<sup>40</sup> using Dunning's cc-pVTZ basis.<sup>30</sup> This choice has been shown in previous investigations to be a good compromise between accuracy and computational cost.<sup>16,17</sup> The quadratic force field has been computed using analytical second derivatives,<sup>41</sup> while the corresponding cubic force field has been obtained through numerical differentiation of analytically evaluated second derivatives as described in refs. 13, 37 and 42.

### C. Vibrational corrections to internuclear distances

The computed harmonic and cubic force fields allow a direct computation of vibrational effects on the internuclear distances. This enables us to provide geometrical parameters which correspond to those that are extracted from the experimental investigations. In particular, we compute the mean internuclear distances ( $r_g$ ) and the distances between the mean positions of the nuclei ( $r_{\alpha}$ ). The required computational expressions are<sup>43</sup>

$$r_g = r_e + \sum_s \gamma_s \langle Q_s \rangle + \frac{1}{2} \sum_{s,t} \gamma_{st} \langle Q_s Q_t \rangle + \dots$$

$$\approx r_e + \sum_s \gamma_s \langle Q_s \rangle + \frac{1}{2} \sum_s \gamma_{ss} \langle Q_s Q_s \rangle \quad (3)$$

$$r_{\alpha} = r_e + \sum_s \gamma_s \langle Q_s \rangle \quad (4)$$

where  $\gamma_s$  and  $\gamma_{st}$  are the first and second derivatives of the internuclear distances with respect to the corresponding normal coordinates evaluated at the equilibrium geometry. Neglecting temperature effects, these quantities are easily computed, as for the vibrational ground state  $\langle Q_r \rangle$  and  $\langle Q_r^2 \rangle$  are given by

$$\langle Q_r \rangle = -\left( \frac{\hbar}{2\pi c \omega_r} \right)^{1/2} \sum_s \phi_{rss} \quad (5)$$

$$\langle Q_r^2 \rangle = \frac{\hbar}{4\pi c \omega_r} \quad (6)$$

while  $\langle Q_r Q_s \rangle$  with  $r \neq s$  vanishes within the harmonic approximation. Note that for the vibrational ground state  $r_{\alpha}$  equals  $r_z$  and thus is directly comparable to the corresponding distances obtained either from spectroscopic or electron diffraction data.

### D. Analysis of experimental rotational constants

With the computed vibrational corrections to the rotational constants (see section IIB), it is possible to correct the experimental rotational constants ( $B_0$  values, from ref. 20–22) of C<sub>3</sub>H<sub>4</sub>, C<sub>3</sub>D<sub>4</sub> and C<sub>3</sub>H<sub>2</sub>D<sub>2</sub> for these effects and to obtain the corresponding equilibrium ( $B_e$ ) values. Those can be used to determine the equilibrium ( $r_e$ ) geometry *via* a least-squares fit. In the fitting procedure, we used the following rotational constants:  $B_0$  for C<sub>3</sub>H<sub>4</sub>,  $B_0$  for C<sub>3</sub>D<sub>4</sub>, as well as  $B_0$  and  $C_0$  for

**Table 1** Calculated and experimental geometries (distances in Å angles in degrees) for allene<sup>a</sup>

		<i>r</i> (C–C)	<i>r</i> (C–H)	<i>α</i> (HCH)
<i>r</i> <sub>0</sub>	exp. <sup>b</sup>	1.3084(3)	1.0872(13)	118.2(2)
<i>r</i> <sub>g</sub>	exp. <sup>c</sup>	1.3129(9)	1.102(2)	
	calc. <sup>d</sup>	1.3131	1.1001	
<i>r</i> <sub>z</sub>	exp. <sup>e</sup>	1.3091(4)	1.0862(10)	118.27(15)
	exp. <sup>c</sup>	1.3093(7)	1.0865(19)	118.3(3)
	calc. <sup>d</sup>	1.3095	1.0846	118.19
<i>r</i> <sub>e</sub>	exp. <sup>c</sup>	1.3082(10)	1.076(3)	118.2(5)
	exp./theor. <sup>f</sup>	1.3069	1.0808	118.35
	calc. <sup>g</sup>	1.3070	1.0800	118.16
	calc. <sup>h</sup>	1.3074	1.0810	118.21

<sup>a</sup> Experimental uncertainties are given in parentheses. <sup>b</sup> Obtained from rotational constants (ref. 18). <sup>c</sup> Obtained from electron diffraction data (ref. 23). <sup>d</sup> CCSD(T)/cc-pVQZ geometry plus vibrational corrections computed at the SDQ-MBPT(4)/cc-pVTZ level. <sup>e</sup> Obtained from rotational constants (ref. 19). <sup>f</sup> Obtained from analysis of the experimental rotational constants (refs. 20–22) corrected by vibrational corrections computed at the SDQ-MBPT(4)/cc-pVTZ level. <sup>g</sup> Optimized at CCSD(T)/cc-pVQZ level. <sup>h</sup> Optimized at CCSD(T)/cc-pCVQZ level.

C<sub>3</sub>H<sub>2</sub>D<sub>2</sub>. The vibrational corrections were used as obtained from the corresponding SDQ-MBPT(4)/cc-pVTZ calculations. The least-squares fit was carried out with respect to the rotational constants. The corresponding weight in the fitting procedure has been set to one for all supplied constants.

## E. Fundamental vibrational frequencies

Fundamental frequencies  $\nu_r$  have been computed using the usual second-order perturbation theory expressions:<sup>36</sup>

$$\nu_r = \omega_r + 2x_{rr} + \frac{1}{2} \sum_{s \neq r} x_{rs} + \sum_t x_{rt} \quad (\text{non-degenerate modes}) \quad (7)$$

$$\nu_r = \omega_r + 3x_{rr} + \frac{1}{2} \sum_s x_{rs} + \sum_{t \neq r} x_{rt} + g_{rr} \quad (\text{degenerate modes}) \quad (8)$$

with the sum over *s* and *t* running over all non-degenerate and degenerate modes, respectively.  $\omega_r$  denotes the harmonic frequencies, while  $x_{rs}$ ,  $x_{rt}$  and  $g_{rs}$  are the usual anharmonicity constants. Explicit expressions for the latter can be found in ref. 36 and are not repeated here. We note only that the determination of the anharmonicity constants requires the knowledge of the quartic force field which we compute by numerical differentiation of analytic second derivatives as described in ref. 13, 37 and 42.

The anharmonic corrections to the vibrational frequencies of the main isotopomer of allene (C<sub>3</sub>H<sub>4</sub>) have been computed at the second-order many-body perturbation theory [MBPT(2)] level using Dunning's cc-pVTZ basis.<sup>30</sup> Improved

**Table 2** Calculated and experimental rotational constants (in cm<sup>−1</sup>) for allene<sup>a</sup>

		Experiment	Experiment plus calculated vibrational corrections	Calculations
C <sub>3</sub> H <sub>4</sub>	<i>A</i> <sub>e</sub>		4.852 9869 <sup>f</sup>	4.871 255 76 <sup>g</sup> 4.859 625 30 <sup>h</sup> 0.297 290 94 <sup>g</sup> 0.297 080 45 <sup>h</sup>
	<i>B</i> <sub>e</sub>		0.297 386 58 <sup>f</sup>	
	<i>A</i> <sub>0</sub>	4.807(8) <sup>b</sup> 4.8116(14) <sup>c</sup> 4.811 655(11) <sup>d</sup>		4.818 294 07 <sup>e</sup>
	<i>B</i> <sub>0</sub>	0.296 32(6) <sup>b</sup> 0.296 32(2) <sup>c</sup> 0.296 274 87(11) <sup>d</sup>		0.295 968 74 <sup>e</sup>
	<i>A</i> <sub>e</sub> − <i>A</i> <sub>0</sub>			0.041 331 23
	<i>B</i> <sub>e</sub> − <i>B</i> <sub>0</sub>			0.001 111 71
	<i>A</i> <sub>e</sub>		2.429 72 <sup>f</sup>	2.437 456 16 <sup>g</sup> 2.431 680 51 <sup>h</sup> 0.232 880 96 <sup>g</sup> 0.232 712 93 <sup>g</sup> 2.417 261 94 <sup>e</sup>
	<i>B</i> <sub>e</sub>		0.232 985 <sup>f</sup>	
	<i>A</i> <sub>0</sub>	2.4153(3) <sup>c</sup>		
	<i>B</i> <sub>0</sub>	0.232 14(8) <sup>b</sup> 0.232 14(3) <sup>c</sup> 0.232 153(15) <sup>i</sup>		0.231 881 06 <sup>e</sup>
C <sub>3</sub> D <sub>4</sub>	<i>A</i> <sub>e</sub> − <i>A</i> <sub>0</sub>			0.014 418 57
	<i>B</i> <sub>e</sub> − <i>B</i> <sub>0</sub>			0.000 831 87
	<i>A</i> <sub>e</sub>		3.238 064 <sup>d</sup>	3.249 108 99 <sup>g</sup> 3.241 410 09 <sup>h</sup> 0.266 109 56 <sup>g</sup> 0.265 927 35 <sup>h</sup> 0.259 044 68 <sup>g</sup> 0.258 855 71 <sup>h</sup>
	<i>B</i> <sub>e</sub>		0.266 221 21 <sup>g</sup>	
	<i>C</i> <sub>e</sub>		0.259 126 95 <sup>g</sup>	
	<i>A</i> <sub>0</sub>	3.2137(19) <sup>c</sup> 3.216 624(9) <sup>j</sup>		3.219 970 46 <sup>e</sup> 0.265 060 84 <sup>e</sup> 0.257 812 06 <sup>e</sup> 0.021 439 63 0.000 866 51 0.001 043 65
	<i>B</i> <sub>0</sub>	0.265 354 70 <sup>j</sup>		
	<i>C</i> <sub>0</sub>	0.258 083 30 <sup>j</sup>		
	<i>A</i> <sub>e</sub> − <i>A</i> <sub>0</sub>			
	<i>B</i> <sub>e</sub> − <i>B</i> <sub>0</sub>			
H <sub>2</sub> C <sub>3</sub> D <sub>2</sub>	<i>A</i> <sub>e</sub>			
	<i>B</i> <sub>e</sub>			
	<i>C</i> <sub>e</sub>			
	<i>A</i> <sub>0</sub>	3.2137(19) <sup>c</sup> 3.216 624(9) <sup>j</sup>		3.219 970 46 <sup>e</sup> 0.265 060 84 <sup>e</sup> 0.257 812 06 <sup>e</sup> 0.021 439 63 0.000 866 51 0.001 043 65
	<i>B</i> <sub>0</sub>	0.265 354 70 <sup>j</sup>		
	<i>C</i> <sub>0</sub>	0.258 083 30 <sup>j</sup>		
	<i>A</i> <sub>e</sub> − <i>A</i> <sub>0</sub>			
	<i>B</i> <sub>e</sub> − <i>B</i> <sub>0</sub>			
	<i>C</i> <sub>e</sub> − <i>C</i> <sub>0</sub>			

<sup>a</sup> Experiment uncertainties are given in parentheses. <sup>b</sup> Ref. 18. <sup>c</sup> Ref. 19. <sup>d</sup> Ref. 22. <sup>e</sup> Rotational constants calculated at the CCSD(T)/cc-pCVQZ level plus vibrational corrections computed at the SDQ-MBPT(4)/cc-pVTZ level. <sup>f</sup> Derived from rotational constants (ref. 22, 20 and 21) plus vibrational corrections computed at the SDQ-MBPT(4)/cc-pVTZ level. <sup>g</sup> Rotational constants calculated at CCSD(T)/cc-pVQZ level. <sup>h</sup> Rotational constants calculated at CCSD(T)/cc-pCVQZ level. <sup>i</sup> Ref. 20. <sup>j</sup> Ref. 21.

**Table 3** Calculated harmonic and fundamental frequencies (in  $\text{cm}^{-1}$ ) in comparison with experiment

Mode number	Symmetry	Harmonic MBPT(2)/cc-pVTZ	MBPT(2)/cc-pVTZ	Fundamental MBPT(2) <sup>a</sup> /cc-pVQZ	CCSD(T) <sup>b</sup> /cc-pVTZ	Exp. <sup>c</sup>
1	E	361	365	369	351	352.73
2	E	361	365	369	351	
3	E	881	855	850	851	840.93
4	E	881	855	850	851	
5	B <sub>1</sub>	902	882	880	857	848.59
6	E	1024	1003	998	1005	999.00
7	E	1024	1003	998	1005	
8	A <sub>1</sub>	1106	1093	1092	1078	1072.22
9	B <sub>2</sub>	1450	1409	1401	1411	1359.0
10	A <sub>1</sub>	1501	1456	1446	1457	1442.55
11	B <sub>2</sub>	2054	2012	2014	1985	1959.1
12	A <sub>1</sub>	3201	3074	3064	3040	3006.7
13	B <sub>2</sub>	3202	3077	3067	3044	
14	E	3275	3139	3147	3096	3085.43
15	E	3275	3139	3147	3096	

<sup>a</sup> Harmonic MBPT(2)/cc-pVQZ frequencies plus anharmonic correction computed at the MBPT(2)/cc-pVTZ level. <sup>b</sup> Harmonic CCSD(T)/cc-pVTZ frequencies plus anharmonic correction computed at the MBPT(2)/cc-pVTZ level. <sup>c</sup> Ref. 19.

estimates for the fundamental frequencies have been obtained by combining the MBPT(2)/cc-pVTZ anharmonic corrections with harmonic frequencies calculated either at the MBPT(2)/cc-pVQZ or CCSD(T)/cc-pVTZ level.

All quantum chemical calculations have been carried out with a local version of the ACESII program system.<sup>44,45</sup>

### III. Results and discussion

Table 1 compares our computational results for the  $r_e$ ,  $r_g$  and  $r_0$  geometries with the corresponding experimental results from refs. 18, 19 and 23. In addition, Table 1 reports the  $r_e$  structure obtained in this work using the combined experimental/theoretical approach based on measured rotational constants and computed vibrational corrections. For the  $r_e$  structure, good agreement is obtained between the computational results (CCSD(T)/cc-pVQZ and CCSD(T)/cc-pCVQZ) and the structure derived from rotational constants. Differences amount to less than 0.1 pm for the bond distances and 0.1° to 0.2° for the bond angle. This is within the accuracy which both the CCSD(T) calculation and the analysis of rotational constants can provide.<sup>16</sup> Differences between geometrical parameters obtained at the CCSD(T)/cc-pVQZ and CCSD(T)/cc-pCVQZ levels are also small with the CCSD(T)/cc-pCVQZ bond distances slightly longer and in a slightly better agreement with the parameters derived from the rotational constants. Table 1 also shows the  $r_e$  structure obtained from electron diffraction data.<sup>23</sup> Agreement with the present results is satisfactory, though the deviations are somewhat larger. However, this is in line with the larger error bars connected with these values. Nevertheless, we note that the CC distance derived from the electron diffraction data seems to be slightly too long (by 0.001 to 0.002 Å) and the CH distance slightly too short (by 0.004 to 0.005 Å).

Based on the good agreement between the geometrical parameters obtained from the analysis of rotational constants using computed vibrational corrections and the pure computational results obtained at the CCSD(T) level using either the cc-pVQZ or the cc-pCVQZ basis set, we recommend for allene the following  $r_e$  structure:  $r_e(\text{CC}) = 1.307 \pm 0.001$  Å,  $r_e(\text{CH}) = 1.081 \pm 0.002$  Å,  $\alpha_e(\text{HCH}) = 118.3^\circ \pm 0.1^\circ$ .

In addition to the  $r_e$  structures, Table 1 also shows the  $r_g$  and  $r_z$  geometries. As the comparison of these different types of geometrical parameters indicates, vibrational effects are not negligible, *i.e.*, about 0.006 Å for the CC distance and about 0.02 Å for the CH distance. Agreement between the computational results and those obtained from experiment is, for the

vibrationally averaged distances, satisfactory, thus indicating that experiment and theory provide a consistent description for the geometry of allene. For the  $r_g$  parameters obtained from electron diffraction, good agreement is also obtained for the non-bonded internuclear distances.<sup>46</sup>

Table 2 summarizes the computed and experimental rotational constants for the three considered allene isotopomers and thus supplies the information required for the least-squares fit. We note that for the  $B_0$  and  $C_0$  constants good agreement has been obtained between theory and experiment (about 0.05% deviation), while as expected the discrepancy is somewhat larger for the  $A_0$  constants (about 0.35% deviation). The larger uncertainties in the  $A_0$  constants are also the reason why these constants have not been considered in the least-squares fit procedure.

Table 3 finally gathers experimental and calculated vibrational frequencies for allene. To allow for rigorous comparison with the experimental data given in ref. 19, fundamental frequencies as outlined in section II E have been computed. The anharmonic corrections to the frequencies amount to a few wavenumbers for the low-frequencies mode but to more than 100  $\text{cm}^{-1}$  for the CH stretching modes. Inclusion of anharmonic effects systematically improves the agreement between theory and experiment. Some further improvement is noted when the anharmonic corrections computed at the MBPT(2)/cc-pVTZ level are combined with harmonic frequencies obtained either at the MBPT(2)/cc-pVQZ or the CCSD(T)/cc-pVTZ level. However, the remaining error is still substantial and ranges from 10  $\text{cm}^{-1}$  for the low-frequency modes up to more than 50  $\text{cm}^{-1}$  for the high-frequency modes. Limitations of the second-order perturbation theory treatment based on a quartic force field are most likely the reason for the remaining discrepancies between theory and experiment.

### IV. Summary

As demonstrated in the present work for allene, the combined use of experiment and theory enables the accurate determination of equilibrium geometries in a rather straightforward manner. In the approach used here, accurate values for the structural parameters are obtained from the analysis of experimental rotational constants which have been corrected for vibrational effects by means of quantum chemical calculations. As the corresponding calculations of the vibration-rotation interaction constants is a fairly routine issue, provided analytic second derivatives are available, and as for many smaller molecules rotational constants are either available in the liter-



ature or accessible *via* rotational spectroscopy, it is expected that this combined use of experiment and theory will significantly increase our knowledge of accurate molecular structures. This will not only be the case for standard organic compounds as shown in this work, but also for more exotic compounds (*e.g.*, cumulenic carbenes,<sup>38</sup> silicon–carbon clusters,<sup>47,48</sup> *etc.*) for which rotational constants are available due to their astrophysical importance.

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