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# Stability and properties of C<sub>4</sub> isomers

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The relative electronic energies of the  $^1A_g$  rhombus and the  $^3\Sigma_g^-$  linear isomers of C<sub>4</sub> have been computed using a  $5s3p1d$  basis at various levels of coupled-cluster and many-body perturbation theory. At the highest level performed, CCSD + T(CCSD), the two isomers are essentially isoenergetic. Thermodynamic results indicate, however, that the linear isomer will be significantly more abundant in the plasma in which C<sub>4</sub> is formed. Vibrational frequencies are presented and compared with experimental results; some of the prior assignments are questioned. The isotropic ESR hyperfine splitting parameters for the linear triplet state have been computed and are also compared with experimental results. Finally, the ionization potential and electron affinity for both structures are presented.

## I. INTRODUCTION

Small carbon clusters have been predicted to exist in the atmospheres of carbon stars<sup>1,2</sup> and in terrestrial laboratories they have been shown to exist in graphite vapor through mass-spectrometric determinations.<sup>3-5</sup> Of these clusters, only the carbon atom, C<sub>2</sub> and C<sub>3</sub> species, have been well characterized.

The linear form of C<sub>4</sub> was predicted to be a  $^3\Sigma_g^-$  state with the electronic configuration:

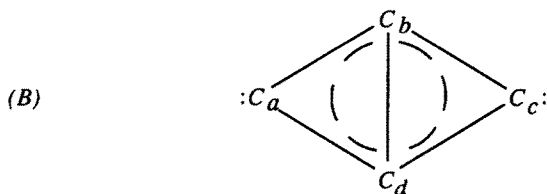
$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 3\sigma_u^2 4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 1\pi_u^4 1\pi_g^2$$

and the corresponding cumulenenic structure:



based on semiempirical calculations by Pitzer and Clementi in 1959,<sup>6</sup> and later on minimum basis *ab initio* SCF calculations by Clementi.<sup>7</sup> The cyclic form, which was first proposed by Slanina and Zahradnik<sup>8</sup> on the basis of MNDO/2 calculations, is a rhombus and has the electronic configuration

$1a_g^2 1b_{3u}^2 2a_g^2 1b_{2u}^2 3a_g^2 2b_{2u}^2 3a_g^2 2b_{3u}^2 2b_{2u}^2 4a_g^2 1b_{1g}^2 1b_{1u}^2 3b_{3u}^2 5a_g^2$ .  
*Ab initio* results yielded additional support for this cyclic structure.<sup>9</sup> Its electronic structure may be represented formally as



based on calculations by Magers, Harrison, and Bartlett<sup>10</sup> (MHB).

Recent *ab initio* results from Raghavachari and Binkley<sup>11</sup> on  $n = 2-10$  carbon clusters show an alternation of stability in which the linear form is more stable for odd  $n$ , but the cyclic form is lower for even  $n$ . Theoretical studies of C<sub>4</sub>, however, have shown the two isomers lie fairly close in ener-

gy,<sup>9-12</sup> and the question of which isomer is actually the ground state may have consequences in the general understanding of clusters of carbon and other atoms.

Experimental work on neutral C<sub>4</sub> is relatively scarce. In a series of ESR and optical studies,<sup>13-15</sup> and a more recent study which also includes C<sub>4</sub>,<sup>16</sup> Weltner and co-workers have studied the molecule by trapping it in inert gas matrices. Their ESR observations are attributed to the  $^3\Sigma_g^-$  linear structure of C<sub>4</sub>. The observed electronic and vibrational transitions were assigned to the linear triplet as well, but it should be noted that at that time there was no evidence for the rhombic form.

Photoelectron spectra of C<sub>n</sub><sup>-</sup> obtained by Smalley and co-workers<sup>17</sup> show no evidence of a cyclic structure before C<sub>10</sub><sup>-</sup>, although the stabilities of the C<sub>4</sub> anions may differ significantly from those of the neutral isomers.

In this paper we examine the relative stability of the linear and rhombic structures [(A) and (B), respectively] of C<sub>4</sub> based on electronic energy, with and without the inclusion of thermodynamic effects. Theoretical vibrational frequencies are also reported, and the correspondence with experimental frequencies is discussed. In addition, we report the vertical ionization potential and electron affinities of both species and the ESR hyperfine splitting constants of the linear form in order to provide a basis for comparison with experimental results.

## II. COMPUTATIONAL PROCEDURES

The calculations used a  $5s3p1d$  basis consisting of Dunning's (9s5p/5s3p) set<sup>18</sup> augmented by the polarization function ( $d$  exponent = 0.654) of Redmon, Purvis, and Bartlett.<sup>19</sup> This gave a basis of 120 uncontracted functions, or a contracted [5s3p1d] set comprising 80 basis functions.

The SCF calculations in this work use a single-configuration RHF wave function to represent closed-shell singlet states and a single-configuration UHF wave function for open-shell states. The only exceptions to this are the restricted open-shell Hartree-Fock (ROHF) calculations of the relative electronic energies and SCF vibrational frequencies of the triplet ground state of the linear isomer.

Correlation effects have been included by many-body perturbation theory (MBPT)<sup>20–22</sup> and coupled cluster (CC) methods<sup>20,23–25</sup> through the CCSD + T(CCSD) model. This latter model accounts for all single and double excitations and also includes the dominant effects of triple excitations.<sup>10,26,27</sup>

Although spin contamination is a well known problem with UHF wave functions, it has been shown empirically that the CCSD level of theory removes most of the spin contaminant of the UHF reference and that inclusion of triple excitations further reduces spin contamination.<sup>28,29</sup> A formal proof that CCSD benefits from annihilation of the lowest spin contaminant has been given.<sup>30</sup> For the C<sub>4</sub> triplet state the unimportance of spin contamination has been verified by using our recently proposed ROHF based CC calculations which suffer less from spin contamination.<sup>31</sup> As expected, they correspond quite closely with the UHF based CC results at the highest levels of theory.

The only new vibrational frequencies presented in this work are limited to the SCF level of theory. All of them were obtained by analytical SCF second derivatives. The UHF infrared intensities presented were obtained by analytical first derivatives of the SCF dipole moment.

Spin densities have been computed by finite field methods, as described by Sekino and Bartlett.<sup>32</sup> The isotropic hyperfine coupling constant is given by

$$\hat{a}_N = \frac{8\pi}{3} \frac{g_e}{g_0} g_N \beta_N \hat{\rho}(r_N), \quad (1)$$

and the spin density operator in second quantization is

$$\hat{\rho}(r_N) = S_z^{-1} \sum_{p,q} \langle \phi_p | \hat{S}_z \delta(r - r_N) | \phi_q \rangle p^\dagger q, \quad (2)$$

where  $p$  and  $q$  run over all orbitals. In these expressions, the term  $g_e/g_0$  is the ratio of the  $g$  values for the free electron and the molecule under consideration and is taken to be unity in these calculations<sup>33</sup>;  $g_N$  and  $\beta_N$  are the nuclear magnetogyric ratio and nuclear magneton, respectively. Applying the perturbation to a particular nucleus  $N$ , the spin density is given by

$$\hat{\rho}(r_N) = \frac{E_\mu - E_{-\mu}}{2\mu}, \quad (3)$$

where  $\mu$  is the field parameter, chosen to be  $\pm 0.0005$ . This value gives excellent agreement with analytic determinations of the density matrix<sup>34</sup> which have recently become available. The relative energy and spin density calculations correlated all orbitals, including inner shells.

The ionization potentials and electron affinities were computed by taking the difference between the energies of the neutral and the appropriate ion without relaxing the geometry of the ion. For these calculations the four 1s orbitals and their corresponding virtuals (eight MOs total) were frozen to substitution.

All calculations were performed at the MBPT-D(4)/4s2p1d geometry obtained by MHB which is given along with their SCF/4s2p1d geometry in Table I.

To estimate the effects of finite temperatures on the relative stabilities of the isomers, thermodynamic functions were evaluated using statistical thermodynamic methods<sup>35</sup> using

TABLE I. Optimum geometries of C<sub>4</sub> isomers. Bond lengths are in Å and angles in degrees. From Ref. 10 (4s2p1d basis).

Structure	Bond or angle	SCF	D-MBPT(4)
Linear	<i>a</i> - <i>b</i>	1.308	1.330
	<i>b</i> - <i>c</i>	1.283	1.305
Rhombic	<i>a</i> - <i>b</i>	1.435	1.460
	<i>b</i> - <i>d</i>	1.475	1.530
	< <i>a</i> - <i>b</i> - <i>c</i>	118.15	116.80
	< <i>d</i> - <i>a</i> - <i>b</i>	61.85	63.20

the program PLOTGIBB.<sup>36</sup> Rotational and vibrational contributions to the partition function were obtained with the rigid rotor-harmonic oscillator approximation using the MBPT(2)/6-31G\* harmonic vibrational frequencies obtained by Michalska and co-workers.<sup>37</sup> Contributions from the low-lying electronic states of the linear form have been neglected since they would favor the linear isomer, affecting only the exact numbers, not the qualitative effects of finite temperature.<sup>16</sup>

### III. RESULTS AND DISCUSSION

#### A. Relative stabilities and thermodynamic effects

The computed energies of each isomer, using a 5s3p1d basis, are shown in Table II. Also shown are the individual contributions of triple and quadruple excitations in fourth-order perturbation theory and the T(CCSD) contribution arising from partial inclusion of triples in coupled cluster theory. These individual contributions follow much the same pattern seen for the 4s2p1d basis in the work of MHB. It is clear that triple excitations have an important contribution to the total energy of the molecules, and triples in perturbation theory tend to exaggerate the difference between the two isomers when compared with the coupled cluster result.

In Table III the relative electronic energies are compared for the 5s3p1d basis and the 4s2p1d basis from MHB. The main difference between the present work and that of MHB is that the larger basis set favors the linear isomer by

TABLE II. Ground state energies of C<sub>4</sub> isomers at various levels of theory(5s3p1d basis).

Level	Ground state energy (a.u.)	
	Linear	Rhombus
SCF	-151.211 78	-151.169 83
D(2)	-151.715 40	-151.736 91
D(4)	-151.758 39	-151.762 21
SD(4)	-151.768 79	-151.769 94
SDQ(4)	-151.754 29	-151.750 83
Q(4)	+0.014 49	+0.019 11
SDTQ(4)	-151.781 71	-151.790 59
T(4)	-0.027 42	-0.039 77
CCSD	-151.756 51	-151.750 89
CCSD + T(CCSD)	-151.788 88	-151.786 80
T(CCSD)	-0.032 37	-0.035 90

TABLE III. Comparison of relative electronic energies [ $E(^3\Sigma_g^-) - E(^1A_g)$ ] (in kcal mol<sup>-1</sup>) for 4s2p1d and 5s3p1d basis sets. 4s2p1d basis results from Ref. 10.

Level	Relative energy (kcal/mol)	
	4s2p1d	5s3p1d
SCF	-20.66	-26.32
D(2)	18.91	13.50
D(4)	7.91	2.40
SD(4)	6.30	0.72
SDQ(4)	3.71	-2.18
SDTQ(4)	10.75	5.57
CCSD	2.45	-3.52
CCSD + T(CCSD)	4.49	-1.31
CCSDT-1	5.01	-0.49 <sup>a</sup>

<sup>a</sup> The CCSDT-1 result for the 5s3p1d basis is estimated. See the text.

$5.5 \pm 0.3$  kcal mol<sup>-1</sup> at all levels of correlation studied. This confirms the suggestion by MHB that larger basis sets than 4s2p1d and even 5s3p1d will be necessary to unambiguously determine the true ground state of C<sub>4</sub>.

At the highest level calculation in this work, the linear isomer is found to be roughly 1 kcal mol<sup>-1</sup> more stable than the rhombic structure. Making use of the shift in relative energies on increasing the size of the basis set, we estimate that the relative electronic energies at the CCSDT-1 level would be  $-0.5 \pm 0.3$  kcal mol<sup>-1</sup> for the 5s3p1d basis. This difference is zero within the expected accuracy of the calculation; hence, the two isomers are essentially isoenergetic when a 5s3p1d basis is used.

ROHF based CC calculations were used to check the extent of spin contamination of the linear triplet state. At the CCSD + T(CCSD) level, the relative energy was -1.22 kcal mol<sup>-1</sup>. This compares quite well with the value obtained using a UHF reference for the linear isomer, indicating that spin contamination is not a problem in the UHF/CC calculations.

The zero-point energies of the two species, given in Table IV, are also essentially equal and thus have no effect on the relative energies. Table IV also shows the thermodynamic functions for the two isomers evaluated at STP (298.15 K, 1 atm) and at roughly the conditions in which C<sub>4</sub> is formed

TABLE IV. Zero point vibrational energies, statistical thermodynamic properties, and relative concentrations of the isomers of C<sub>4</sub> at STP and 4000 K.

Property	Linear		Rhombus	
	298.15 K	4000 K	298.15	4000 K
<i>E</i> (kcal/mol)	11.04	76.23	11.78	73.40
<i>H</i> (kcal/mol)	11.63	84.18	12.38	81.35
<i>G</i> (kcal/mol)	-6.54	-350.10	-5.31	-334.33
<i>S</i> (cal/mol deg)	60.93	108.57	59.34	103.92
Relative concentration	7.8	7.3	1	1
Zero point energy (kcal/mol)	8.43		8.36	

from laser vaporization of graphite (400 K, 1 atm). The resulting values for the rhombus=linear equilibrium are also presented. As the temperature increases, the free energy increasingly favors the linear structure; and, in the graphite vapor, the linear isomer is roughly 15 kcal mol<sup>-1</sup> more stable. This  $\Delta G$  corresponds to a  $K_p$  of roughly 7; and, as pointed out by Van Zee *et al.*,<sup>16</sup> implies that the rhombic isomer will compose only 10%–15% of the C<sub>4</sub> formed. This concentration will decrease if the electronic energies further favor the linear species, but it is not apparent that calculations with larger bases and higher levels of theory than were used in this work would favor the linear isomer.

## B. Vibrational frequencies

Although little experimental work exists on C<sub>n</sub> species, two vibrational frequencies have been assigned to C<sub>4</sub>. The asymmetric stretching frequency of the ground state was assigned a value of 2164 cm<sup>-1</sup> in the 1971 work of Thompson, *et al.*,<sup>14</sup> and a value of  $2100 \pm 10$  cm<sup>-1</sup> was given for the symmetric stretching frequency of an excited state in the 1976 work of Graham *et al.*<sup>15</sup> Both of these assignments assumed that C<sub>4</sub> is linear.

In recent years theoretical studies for the vibrational frequencies of both the linear and the rhombic isomers of C<sub>4</sub> have been made so that a comparison with those experimental values might aid the experimental identification of C<sub>4</sub>. Unfortunately, two of these studies have been limited to the SCF level of theory.<sup>12,38</sup> SCF vibrational frequencies are generally found to be too high by roughly 10–15% when compared to experimental values because SCF theory overestimates the strength of bonding. Both of these SCF vibrational frequency calculations used a 6-31G\* basis set and UHF theory for the open-shell <sup>3</sup>Σ<sub>g</sub><sup>-</sup> ground state of the linear isomer. Both studies yielded essentially the same values. Those values are listed in Table V along with our own UHF and ROHF vibrational frequencies for the linear isomer computed with the 4s2p1d basis set described by MHB.

There are two reasons for introducing more SCF C<sub>4</sub> vibrational frequencies into the literature. The first reason is to compare our UHF/4s2p1d values with the UHF/6-31G\* values. Note that all three sigma vibrational frequencies are slightly lowered with the 4s2p1d basis set. We should point out that the 6-31G\* set is 3s2p1d in terms of the number of functions and uses the same exponents for both *s* and *p* functions, thereby making it less flexible than the 4s2p1d basis.

TABLE V. SCF harmonic vibrational frequencies for the linear isomer in cm<sup>-1</sup>. Corresponding intensities in parentheses, in km mol<sup>-1</sup>. UHF-6-31G\* results from Refs. 11 and 12.

Symmetry	UHF/6-31G*		ROHF/4s2p1d	
	UHF/6-31G*	UHF/4s2p1d	UHF/4s2p1d	ROHF/4s2p1d
Σ <sub>g</sub> <sup>+</sup>	2345	2300	(0.0)	2292
Σ <sub>u</sub> <sup>+</sup>	1741	1715	(151.8)	1349
Σ <sub>g</sub> <sup>+</sup>	1022	1003	(0.0)	1014
Π <sub>g</sub>	408	454	(0.0)	449
Π <sub>u</sub>	209	214	(22.7)	209

The second reason for presenting new SCF frequencies is also one of comparison. We have computed the SCF vibrational frequencies for the linear isomer using both UHF and ROHF theory. Note that all values are within 11 cm<sup>-1</sup> except for the IR active asymmetric stretch. The values for this frequency differ by over 350 cm<sup>-1</sup>. One might expect UHF theory to better describe stretching frequencies than ROHF theory because UHF theory better handles dissociation, but this singular difference is somewhat surprising. Another possible reason for this difference is the difference in the respective geometries. The UHF frequency calculation was done at the UHF geometry given in Table I. The ROHF frequency calculation was performed at the ROHF optimum geometry in which the bonds are closer to the same length:  $d(C_a - C_b) = 1.300 \text{ \AA}$  and  $d(C_b - C_c) = 1.288 \text{ \AA}$ .

The first correlated calculation of the rhombic frequencies are the MBPT(2) values obtained using a 4s2p1d basis set which were presented by MHB in 1986. These values were calculated using MBPT(2) analytical second derivatives.<sup>39,40</sup> Recently, accurate theoretical frequencies for the linear isomer have been reported by Michalska *et al.* They calculated harmonic vibrational frequencies for both the  $^3\Sigma_g^-$  ground state of the linear isomer and the  $^1A_g$  ground state of the rhombic isomer at the MBPT(2) level with a 6-31G\* basis set. Their values were obtained with MBPT(2) analytical first derivatives<sup>41</sup> and numerical second derivatives. All of these correlated frequencies are presented in Table VI.

Even though the 4s2p1d results should be slightly better due to the increased flexibility mentioned earlier, comparison shows little difference between the two sets of rhombic values. Thus we used the 6-31G\* values in our thermodynamic calculations of the previous section because both isomers were treated at the same level of computation.

From examination of the rhombic frequencies, it is clear that they are all too low to be candidates for the 2164 cm<sup>-1</sup> experimental value. MBPT(2) frequencies are usually within 5% of experimental values and are also generally too high rather than too low.<sup>42,43</sup> Though the  $\Sigma_g^+$  frequency of the linear isomer has a value close to the experimental frequency, it is not IR active. The antisymmetric stretch is calculated to be 1586 cm<sup>-1</sup> and is thus out of range. Therefore, it is

natural to assume that the 2164 cm<sup>-1</sup> frequency comes from a molecular species other than C<sub>4</sub>. In fact, recent experiments using isotopic substitution definitely assign the 2164 cm<sup>-1</sup> frequency to C<sub>5</sub>.<sup>44</sup>

The study of Thompson *et al.* which originally assigned the 2164 cm<sup>-1</sup> line to C<sub>4</sub> also assigned a line at 1544 cm<sup>-1</sup> to C<sub>5</sub>. We agree with Michalska *et al.* that this frequency might correspond to the 1586 cm<sup>-1</sup> calculated value for C<sub>4</sub>. Although SCF frequencies for linear C<sub>5</sub> have been computed,<sup>11</sup> correlated frequencies for C<sub>5</sub> would be helpful to settle the assignment.

The other C<sub>4</sub> experimental frequency of  $2100 \pm 10 \text{ cm}^{-1}$  was assigned to the symmetric stretch of an excited state. One may view the transition from the  $^3\Sigma_g^-$  ground state to the lowest  $^3\Pi_u$  excited state as the transfer of an electron from the nearly nonbonding  $4\sigma_u$  orbital into the  $1\pi_g$  orbital which would lead to a decrease in the central bond and an increase in the outer bonds. A similar change in bonding would occur in the transition from the ground state to the  $^3\Sigma_u^-$  excited electronic state. This transition may be viewed as the transfer of a  $1\pi_u$  electron which is strongly bonding between the central carbon pair into the  $1\pi_g$  orbital. Thus the bonding in either of these excited states would more closely resemble



than it would structure (A). The symmetric stretch is calculated to be 2149 cm<sup>-1</sup> for the ground state, but the actual experimental value would probably be below 2100 cm<sup>-1</sup>. Therefore the higher value of  $2100 \pm 10 \text{ cm}^{-1}$  for the symmetric stretch in the excited state is reasonable.

### C. Spin densities

In Table VII we present the computed spin densities (ESR hyperfine splitting constants) of the linear triplet state to which Weltner and co-workers attribute their observed spectra. Van Zee and co-workers<sup>16</sup> report the parallel and perpendicular components of the hyperfine splitting of C<sub>4</sub> in a neon matrix. Assuming that the spins are predominantly on a single pair of carbon atoms since only a triplet pattern was observed, these values yield an isotropic hyperfine splitting constant ( $|A_{\text{iso}}| = |2A_{\parallel} + A_{\perp}|/3$ ) of 8.4 or 5.3 G, depending upon the signs of the parallel and perpendicular components. Because of the relatively low zero-field split-

TABLE VI. MBPT(2) harmonic vibrational frequencies in cm<sup>-1</sup> for both isomers. Corresponding intensities given in parentheses, in km mol<sup>-1</sup>. 6-31G\* results from Ref. 37. 4s2p1d results from Ref. 10.

Linear			Rhombus <sup>a</sup>		
Symmetry	6-31G*		Symmetry	6-31G*	4s2p1d
$\Sigma_g^+$	2149	(0.0)	$B_{3u}$	1428	(1262.4)
$\Sigma_u^+$	1586	(488.3)	$A_g$	1298	(0.0)
$\Sigma_g^+$	951	(0.0)	$B_{1g}$	1103	(0.0)
$\Pi_g$	419	(0.0)	$A_g$	934	(0.0)
$\Pi_u$	187	(33.3)	$B_{2u}$	712	(184.5)
			$B_{3u}$	374	(316.1)
					359

<sup>a</sup> The rhombic isomer is assumed to lie in the xy plane.

TABLE VII. Spin density (in a.u.) and isotropic hyperfine splitting constant (in Gauss) for the inner and outer carbon atoms of the linear isomer.

Level	Spin density (a.u.)		Isotropic hyperfine splitting (G)	
	Inner	Outer	Inner	Outer
SCF	-0.0218	0.0337	-8.78	13.51
D(2)	-0.0134	0.0226	-5.37	9.07
D(3)	-0.0184	0.0184	-7.37	7.39
D(4)	-0.0175	0.0159	-7.00	6.36
SD(4)	-0.0172	0.0133	-6.89	5.35
SDQ(4)	-0.0178	0.0125	-7.14	5.00

ting parameter,  $|D| = 0.024 \text{ cm}^{-1}$ , which depends largely on electron dipole-dipole interactions which vary as  $\langle r^{-3} \rangle$ , these authors considered most of the spin density to be on the outer two carbon atoms. The MBPT-SDQ(4) values, for both the inner and outer pairs of carbon atoms, agree in magnitude with the observed constants and therefore with the essential finding that the unpaired spins have only a small *s* character. The MBPT-SDQ(4) value for this hyperfine splitting is 5.00 G. The results of Sekino and Bartlett<sup>32</sup> that consider effects of triple excitations and infinite-order coupled-cluster corrections, indicate that the theoretical results could have a fairly large uncertainty so that experiment and theory are in reasonable agreement. The computed hyperfine splittings for the two pairs of atoms are essentially the same in magnitude, giving splitting patterns which overlap. This possibility may explain the inability of Weltner and co-workers to resolve a splitting for the inner pair of atoms.<sup>15</sup>

Several observations may be made regarding the computed splitting constants. First, we must point out the lack of reliability of the SCF level of theory for obtaining good spin densities: in both this work and that of Sekino and Bartlett, there are cases where the SCF spin densities compare well with experiment and others where they are in error (when compared to experimental or high-level theoretical results) by as much as a factor of 2. This should stand as a caution against using only an SCF wave function to obtain spin densities. Sekino and Bartlett also noted that infinite-order effects of coupled cluster theory can be extremely important in obtaining good spin densities if the wave function has a bad spin multiplicity. Since spin contamination does not seem to be a problem for this case, it is expected that the finite order MBPT will provide good results. Finally, although the MBPT-SDQ(4) level has been demonstrated to give relatively good isotropic hyperfine splittings, the available data on the C<sub>6</sub>, C<sub>8</sub>, and C<sub>10</sub> clusters<sup>16</sup> suggests that their splittings may change by only a few Gauss from one to the next. Such resolution is beyond the accuracy of these calculations. This suggests that a more complete treatment of the hyperfine splitting may be required, perhaps including the magnetic dipole terms  $A_{\text{dip}}$ .<sup>45</sup>

#### D. Ionization potentials and electron affinities

The vertical ionization potentials and electron affinities of the two isomers are compared in Table VIII. The rhombic IP computed here is in reasonable accord with the value of

TABLE VIII. Vertical ionization potentials and electron affinities for linear and rhombus isomers in eV.

Level	Ionization potential		Electron affinity	
	Linear	Rhombus	Linear	Rhombus
SCF	10.68	11.11	2.10	1.68
D(2)	10.93	11.39	3.61	1.82
D(3)	10.88	11.44	3.32	1.95
D(4)	10.81	11.42	3.34	1.93
SD(4)	10.80	11.40	3.37	1.98
SDQ(4)	10.86	11.47	3.29	2.02

10.5 eV reported by Raghavachari and Binkley<sup>11</sup> for the adiabatic IP. The discrepancy indicates the importance of geometric relaxation to the ionization process. The electron affinities differ significantly for the two isomers, suggesting that the anions of the two isomers may be distinctly separated in energy. Larger basis sets would be required to get highly accurate electron affinities.

#### IV. CONCLUSIONS

It has been shown that with a 5s3p1d basis set the rhombic and linear isomers of C<sub>4</sub> are essentially isoenergetic, although a still larger basis will be required to unambiguously determine which structure is in fact the ground state. Thermodynamics, however, favors the linear structure by a significant amount under the conditions in the graphite vapor where C<sub>4</sub> is usually formed. The rhombus will compose only 10%–15% of the C<sub>4</sub> in the vapor. Consequently, experiments performed thus far are unlikely to have observed spectral features due to the rhombic structure, as Van Zee *et al.*<sup>16</sup> have pointed out.

These calculations indicate the 2164 cm<sup>-1</sup> IR-active frequency cannot be assigned to linear C<sub>4</sub> and that the observed 1544 cm<sup>-1</sup> frequency is probably the correct assignment.

The hyperfine splittings are in good agreement with experiment, confirming the small amount of *s* character of the unpaired spins.

Finally, the ionization potentials and electron affinities have been presented in the hope of aiding and encouraging further experimental work on the C<sub>4</sub> isomers.

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