

Ab initio study of the structure, infrared spectra, and heat of formation of C₄

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The lowest-lying 1A_g and $^3\Sigma_g^-$ states of C₄ have been studied using basis sets including *f* functions, quadratic configuration interaction, and full fourth-order Møller–Plesset perturbation theory with multiple spin projection. Basis set effects on the linear-cyclic separation have been found to be fairly significant. Use of the 6-311G* and [5s3p1d] basis sets leads to qualitatively different conclusions; this problem is remedied by expansion of the polarization space. At the highest level of theory considered, the cyclic structure lies about 1 kcal/mol below the linear structure. A G1-type estimate of its heat of formation at 0 K of 249.6 kcal/mol is proposed. This value is in disagreement with the generally quoted experimental values, but in good agreement with third-law values by Drowart *et al.* [J. Chem. Phys. **31**, 1131 (1959)] corrected for improved partition functions. Geometries and harmonic frequencies are reported. It is tentatively suggested that a matrix ir band at 1284 cm⁻¹ may belong to cyclic C₄; to aid experimentalists in confirming or rejecting this assignment, theoretical isotope shifts are reported.

I. INTRODUCTION

Over the last few decades, carbon clusters have aroused a lot of interest both theoretically and experimentally; the review by Weltner and Van Zee¹ extends up to April 1989. Additional progress, made since that review, includes the characterization of linear C₄ and C₅ by an interaction between theoretical²⁻⁶ and experimental⁷⁻¹⁰ groups. Very recently, independent *ab initio*¹¹ and semiempirical¹² studies have been carried out that propose a revised assignment of the matrix ir bands^{13,14} of the linear species up to and including C₉. At least for C₇ and C₉, the assignment has been confirmed experimentally by the Berkeley group.¹⁵

In the course of this, an *ad hoc* modification of the modified neglect of diatomic overlap (MNDO)¹⁶ method has been developed that allows very accurate predictions of the harmonic frequencies for the linear species.¹² Unfortunately, results for the cyclic species are much less reliable because the minimal basis set on which all current semiempirical models are built does not have the flexibility to describe highly strained rings.

The ground state structure of C₄ has long since been a matter of controversy. As early as 1977, it was proposed on the basis of a semiempirical MINDO/2 study¹⁷ that C₄ might have a cyclic ground state. A subsequent *ab initio* study by the Pople group¹⁸ at the MP4(SDQ) (Ref. 19) level with a 6-31G* basis set^{20,21} revealed that the linear

$^3\Sigma_g^-$ and rhombic 1A_g states of C₄ are close together in energy: from an isogyric comparison with triplet methylene, they predicted the rhombus to be about 5 kcal/mol lower in energy.

Ritchie *et al.*²² studied the two states at the CISD (configuration interaction with all single and double excitations) level with a Davidson correction,²³ the Huzinaga–Dunning (9s5p1d)/[4s2p1d] basis set^{24,25} (henceforth denoted DZP) was used. They found the two states to be essentially isoenergetic, with the linear state about 0.2 kcal/mol lower in energy. However, triple excitations, which are very important for this type of molecule, are not included at this level of theory.

Magers *et al.* (MHB)²⁶ studied the molecule with the same basis set at the MP4(SDTQ) level,²⁷ as well as with various coupled cluster methods²⁸ up to and including CCSDT-1 (Ref. 29) (coupled cluster with exact inclusion of all single and double substitutions, and approximate inclusion of triple substitutions), at which level they obtained an isomerization energy ΔE of 5.01 kcal/mol (positive values favoring the rhombus).

Raghavachari and Binkley³⁰ (RB) obtained a comparable result at the CCD(ST) level³¹ (coupled cluster with all double substitutions, and a quasiperturbative correction for single and triple excitations). They, however, remarked that because of significant spin contamination in the unrestricted Hartree–Fock (UHF) wave function for the linear species, the actual value would be significantly lower and the two

structures would be very close in energy. MHB made the same remark regarding their own results; however, it has recently been shown that for a single dominant spin contaminant (which is the case for linear C₄), the CCSD (coupled cluster with all single and double substitutions) energy is not affected by the contamination.^{32,33} So the DZP limit will be close to 5 kcal/mol, whereas the 6-31G* limit will be very small. This illustrates that the basis set will have considerable influence on the computed result.

Bernholdt *et al.*³ (BMB) performed a coupled cluster investigation with a [5s3p1d] contraction of the MHB primitive set, which is thus of triple-zeta quality. Their best estimate at that level was -0.49 kcal/mol (favoring the linear). It was further argued on thermodynamical grounds,^{3,34} that the linear structure would be favored anyway at practical temperatures because of the additional degeneracy entropy.

A further study was at the MRD-CI (multireference double excitation configuration interaction)³⁵ level with a DZP basis set by Pacchioni and Koutecký.³⁶ With that method, they found a ΔE of -2.3 kcal/mol; given the fairly small set of reference configurations, this method will only partially include higher excitation effects.

Up to now, the best results (BMB) indicate thus that the two structures will be very close in energy and may coexist even at low temperatures. Concerning the latter, there is a possibility that a 1284 cm⁻¹ matrix ir feature belongs to rhombic C₄.^{11,12} Experimental isotopic substitution data are absent for this band, so the hypothesis cannot be verified directly. Given however the large basis set effects apparently present, it would also be interesting to investigate the system with some larger basis sets of preferably [4s3p2d 1f] quality. Finally, at this level of theory, a theoretical value for the dissociation energy could be obtained through the G1 procedure.³⁷

The purpose of this study is thus threefold:

- (i) to investigate the effect of further basis set extension on the linear-rhombic energy difference;
- (ii) to provide more accurate harmonic frequencies and isotopic substitution data for the rhombic isomer;
- (iii) to obtain a theoretical estimate of the heat of formation of C₄.

II. COMPUTATIONAL METHODS

Most computations were performed using the GAUSSIAN 88 package³⁸ running on the IBM 3090/400e VF at the University of Leuven; some were performed with GAUSSIAN 88 on a VAXstation 3100 under VMS 5.3, as well as using GAUSSIAN 86³⁹ on the IBM/FPS configuration at the Facultés Universitaires de Namur.

Both geometry and frequency calculations (the latter through single numerical differentiation) were carried out at the MP2 level using analytical gradients. The latter are computed with the Pople algorithm⁴⁰ in GAUSSIAN 86, and with the more efficient Z-vector algorithm⁴¹ in GAUSSIAN 88.

For the energy calculations, the recently developed QCISD(T) method⁴² (quadratic configuration interaction, actually an approximation to CCSD with a quasiperturbative triples correction correct to fifth order⁴³) was em-

ployed. This method was recently shown to be near full-CI quality even for some "problem" molecules;⁴⁴ the higher-order terms involving the \hat{T}_1 operator that are neglected compared to full CI normally only matter for very heavy spin contamination or extreme multireference character. The former is absent here; the latter will be discussed at the end of the present paper.

For some of the larger basis set calculations, even QCISD(T) proved to be beyond our computational power. There, MP4 with multiple spin projection as developed by Schlegel^{32,45} was used.

As rigorous size consistency holds for both QCISD(T)⁴² and MP4,⁴⁶ dissociation energies are simply computed by subtracting atomic energies rather than through a supermolecular calculation. This procedure may result in very small errors with singly spin-projected MP4;⁴⁵ however, in the same reference, it was indicated that the problem would be remedied by multiple spin projection.

III. RESULTS AND DISCUSSION

A. Energetics

All total energies (hartree) and isomerization energies ΔE (kcal/mol, plus sign favoring the cyclic) discussed in this section are presented in Table I. (We should point out that quoting energy differences to two decimal places does not imply the computed values to be that accurate. It is only done here to avoid roundoff errors in calculations with these values.)

We first redid the CCD(ST) calculations of RB at the QCISD(T) level, in order to assess the effect of spin contamination on their computed ΔE . The UHF/6-31G* reference geometry, used both here and in RB, was taken from Ref. 18. We see indeed that there is an appreciable effect; the two structures are nearly isoenergetic at the QCISD(T)/6-31G* level. The PMP4 ΔE is relatively close to this value (1.76 kcal/mol off). $\langle \hat{S}^2 \rangle$ values for the linear structure range from 2.20 to 2.22 for all calculations reported in this paper; after a single projection, these values no longer exceed 2.01. This highlights the fact that there is only one major contaminant; QCISD and CCSD should thus do a good job for this molecule as far as being insensitive to spin contamination goes. Application of the second projector changes the total energies by less than a mhartree at the MP4 level; the third changes the energies by only 2 μ hartrees. Only the PMP4(3) energies (those with three projectors) will be reported henceforth in Table I. For the sake of completeness, the four core orbitals were frozen in the correlated calculations (as is standard practice with the Pople basis sets, these not being adequate for core correlation anyway).

Use of a correlated geometry does have a small, but appreciable effect. We redid the just mentioned calculations at the MP2/6-31G* geometry reported by Michalska *et al.*,² to find that the energy difference changes by only +0.08 kcal/mol at the QCISD level, but by +0.66 kcal/mol at the QCISD(T) level. We expect that further optimization of the geometry will result in a very slight additional favoring of the rhombic form.

The fact that the PMP4(3) ΔE values are relatively

TABLE I. Total energies (hartree) and isomerization energy ΔE (kcal/mol) for the $^3\Sigma_g^-$ and 1A_g states of C₄.

Method	$^3\Sigma_g^-$	1A_g	ΔE
RB basis set and geometry			
CCD(ST)/6-31G**	-151.650 00	-151.658 27	5.19
QCISD/6-31G*	-151.633 09	-151.631 06	-1.27
QCISD(T)/6-31G*	-151.657 59	-151.659 28	1.06
MP4/6-31G*	-151.650 09	-151.660 75	6.69
PMP4(1)/6-31G*	-151.656 75	-151.660 74	2.50
PMP4(2)/6-31G*	-151.656 25	-151.660 74	2.82
PMP4(3)/6-31G*	-151.656 25	-151.660 74	2.82
MP2/6-31G* geometry			
QCISD/6-31G*	-151.634 46	-151.63252 ^c	-1.21
QCISD(T)/6-31G*	-151.659 63	-151.66237 ^c	1.72
MHB basis set and geometry			
MP4/[4s2p1d]	-151.663 54	-151.680 66	10.75
PMP4(3)/[4s2p1d]	-151.670 06	-151.680 66	6.65
QCISD/[4s2p1d]	-151.647 21	-151.649 61	1.51
QCISD(T)/[4s2p1d]	-151.671 79	-151.678 53	4.23
CCSD ^b	-151.644 46	-151.648 36	2.45
CCSD + T(CCSD) ^b	-151.671 76	-151.678 92	4.49
CCSDT-1 ^b	-151.671 69	-151.679 67	5.01
MP2/6-311G* geometry			
MP4/6-311G*	-151.701 17	-151.713 70	7.87
PMP4(3)/6-311G*	-151.707 66	-151.713 70	3.79
MP4/[5s3p1d]	-151.705 28	-151.712 97	4.83
PMP4(3)/[5s3p1d]	-151.711 96	-151.712 97	0.63
QCISD/6-311G*	-151.681 17	-151.677 37	-2.39
QCISD(T)/6-311G*	-151.708 52	-151.710 06	0.96
QCISD/[5s3p1d]	-151.685 64	-151.676 90	-5.49
QCISD(T)/[5s3p1d]	-151.712 97	-151.709 47	-2.20
MP4/[5s4p1d]	-151.718 01	-151.727 55	5.99
PMP4(3)/[5s4p1d]	-151.724 70	-151.727 55	1.79
MP4/6-311 + G*	failure	-151.718 86	
PMP4(3)/6-311 + G*	failure	-151.718 86	
MP4/6-311G(2df)	-151.775 99	-151.785 72	6.11
PMP4/6-311G(2df)	-151.782 92	-151.785 72	1.76
MP4/[5s3p2d 1f]	-151.782 41	-151.792 89	6.58
PMP4(3)/[5s3p2d 1f]	-151.789 35	-151.792 89	2.22
eQCISD(T)/6-311G(2df)	-151.783 78	-151.782 08	-1.07
eQCISD(T)/[5s3p2d 1f]	-151.790 36	-151.789 39	-0.61
eQCISD(T)/[5s4p2d 1f]	-151.803 10	-151.803 97	0.55

*Taken from RB (Ref. 30).

^bTaken from MHB (Ref. 26).^cGeometry for 1A_1 state from this work (see footnote to Table II). Energies at geometry from Ref. 2 are QCISD: -151.630 47 and QCISD(T): -151.659 50 hartree. The methods prefixed by an e are extrapolations based on basis set additivity approximations (see the text).

close to the QCISD(T) values comes in handy for the very large basis set calculations.

A second test performed was a comparison with the MHB values. The basis set was DZP, with the polarization exponent $\alpha_D = 0.654$ being taken from MHB. The reference geometries used both here and in MHB were determined at the MP4(D)/DZP level and reported in MHB too. In these calculations, both the four cores and the four highest virtals were frozen. The *d* shell was a full set of six second-order Gaussians.

The MP4 energies were in complete agreement with those reported in MHB, certifying that all basis set, geometry, and electron correlation details are identical.

At the QCISD(T) level, we predict an energy difference of 4.23 kcal/mol, compared to MHB's CCSD + T(CCSD)

(Ref. 47) value of 4.49 kcal/mol and their CCSDT-1 value of 5.01 kcal/mol.

The difference between QCISD and CCSD total energies should normally be a good measure for the reliability of the QCISD method. The QCISD energies are too low by 2.8 and 1.3 mhartrees for the linear and cyclic structures, respectively. The difference between QCISD(T) and CCSD(T) should normally be much smaller; an important subclass of the diagrams in the difference are Hermetian conjugates of diagrams appearing in the quasiperturbative triples part that comes from the singles, and are thus absorbed in QCISD(T) through double counting these contributions.⁴³

Incidentally, the total energies are very close to those obtained at the CCSD + T(CCSD) level. The CCSDT-1

method then, which should give a good estimate of the remaining error, gives a total energy for the linear that is only 100 μ hartrees above our QCISD(T) value, whereas for the cyclic, a difference of about 1 mhartree is seen. We think that the difference between the QCISD(T) and CCSDT-1 energies should normally be a good estimate for the error remaining in the electron correlation treatment; the same assumption was made by BMB in their [5s3p1d] study, where the difference between CCSDT-1 and CCSD + T(CCSD) in the [4s2p1d] basis set was used as a correction term to the CCSD + T(CCSD)/[5s3p1d] difference.

The PMP4 energy difference differs by some 2.4 kcal/mol from the QCISD(T) value, which is still acceptably small. The difference with CCSDT-1 is even less.

Since BMB found that the effect of going from a DZP (double-zeta plus polarization) to a TZP (triple-zeta plus polarization) basis set was rather sizeable, our next step was to consider a triple-zeta basis set. Grev *et al.*⁴⁸ recently showed that the commonly used 6-311G basis set⁴⁹ has two important disadvantages for this purpose: (a) its outer exponents are insufficiently diffuse; (b) the constraint that the *s* and *p* exponents be equal leads to optimized exponents that are actually better suited for the core than for the valence region. The conclusion of these authors was that 6-311G is not of triple-zeta quality, and that a [5s3p] Dunning contraction of Huzinaga's (10s6p) primitive set is to be preferred. We have therefore considered both the 6-311G* basis set and a [5s3p1d] one, based on the Huzinaga/Dunning [5s3p] contracted set and a single five-membered *d* function with $\alpha_d = 0.549$. The latter has been optimized at the MP4(DQ) level for carbon atom in its ground state (frozen core) using the G88OPT utility program bundled with GAUSSIAN 88.

For a reference geometry, we have chosen the MP2/6-311G* level, which yields a good geometry for linear C_3 ,⁵⁰ as a reasonable compromise between quality and computational feasibility. Given the small energy difference to be computed, a higher level of theory for the geometry may have been more desirable; however, it was the best that could be afforded computationally, and the resulting error in ΔE will certainly be negligible against other errors inherent in this treatment. The geometries are reported in Table II.

As seen from Table I, the difference between the two basis sets is indeed quite appreciable. Whereas the [5s3p1d] predicts a difference of -2.20 kcal/mol at the QCISD(T) level, the 6-311G* basis set yields a difference of $+0.96$ kcal/mol; i.e., *the conclusion is even qualitatively affected*.

There is a difference of about 1 kcal/mol between the present QCISD(T)/[5s3p1d] values and the CCSD + T(CCSD)/[5s3p1d] values in BMB. Part of the difference may be due to the different reference geometries; far more importantly, however, the primitive sets are different, the TZP in BMB being a [5s3p1d] contraction from a (9s5p1d) primitive set. (The values for the polarization exponent are also slightly different, but not enough to cause an appreciable difference).

In both cases, the energy difference predicted at the PMP4 level is 2.83 kcal/mol larger than at the QCISD(T) level, compared to 2.42 kcal/mol in the [4s2p1d] basis set

TABLE II. Computed equilibrium geometries (\AA , degrees) for the ${}^3\Sigma_g^-$ and 1A_g states of C_4 .

Method	${}^3\Sigma_g^-$		1A_g	
	r_0	r_i	r	θ
HF/6-31G*	1.2994	1.2758	1.4252	61.50
MP2/6-31G**	1.313	1.296	1.425 ^c	64.60 ^c
MP2/DZP ^b	1.469	63.89
MP4(D)/DZP ^b	1.330	1.305	1.460	63.20
MP2/6-311G*	1.3132	1.2953	1.4575	63.60
MP2/[5s3p1d]	1.3165	1.2992	1.4658	63.91

* Reference 2.

^b Reference 26.

^c Our own results at this level are $r = 1.451$, $\theta = 63.60$ (see the text).

discussed above. Given the rather far-reaching consequences of the transition from DZP to TZP basis sets, the relatively small change in this error is a bit reassuring. If the trend continues, we expect that the difference between PMP4 and QCISD(T) will slightly increase further upon additional expansion of the basis set. As the difference favors the cyclic, using the PMP4 level for the basis set calibration should introduce a slight bias towards the cyclic form.

It should be remarked that the 6-311G* basis set apparently yielded values which are relatively close to the 6-311G*, but not to the [5s3p1d] results.

A further extension which might be considered is the addition of diffuse functions.⁵¹ Their effect is expected to be on the order of 1 kcal/mol for the 6-311G*, but negligible for the [5s3p1d] basis set because the latter's outer exponents are already fairly "diffuse".⁵² Unfortunately, the MP4/6-311 + G* calculation for the linear form failed because of near-linear-dependence effects, leading to exceedingly large MO coefficients which cause a numerically unstable integral transform. The energies obtained beyond the MP2 level are so clearly nonsensical that they are not reported here. At the PMP2 level, it appears that the linear gets a boost of 2.52 kcal/mol, which explains a lot of the discrepancy between the 6-311G* and [5s3p1d] results.

The [5s3p1d] calculations were about the maximum we could computationally afford at the QCISD(T) level. However, as the basis set effects do not appear to have converged yet, we have considered two further extensions of the basis set.

Given the fairly large importance of valence set effects, the first thing we considered was loosening the contraction of the (10s6p) set from [5s3p1d] to [5s4p1d]. The polarization exponent was reoptimized, but could as well have been transferred from the [5s3p1d] calculations: its new value is $\alpha_d = 0.555$. The results show that the cyclic form gets a "push in the back" by 1.16 kcal/mol. Applying this as a correction term to the -2.20 kcal/mol ΔE found at the QCISD(T)/[5s3p1d] level, this leaves only -1.04 kcal/mol favoring the linear, or a nearly isoenergetic situation after applying the correction for QCISD(T) inadequacy.

The second extension considered was of course increasing the polarization space. We have considered both the standard 6-311G(2df) basis set,⁵³ and a [5s3p2d 1f] basis set constructed from the [5s3p1d] basis. In the latter, the *d* exponents were doubled by applying the "even scaling rule" (see Ref. 53 and references there), whereas the *f* exponent was optimized with the same procedure as used above, the [5s3p2d] part being held constant. The α_f thus obtained was 0.775.

The results are a bit surprising, in that the extension of the polarization space favors the linear form by 2.03 kcal/mol in the 6-311G(2df) case, but the cyclic form by 1.59 kcal/mol in the [5s3p2d 1f] case. As a result, the extrapolated QCISD(T)/6-311G(2df) and QCISD(T)/[5s3p2d 1f] values are now in fairly good agreement, being -1.07 and -0.61 kcal/mol, respectively.

In the latter case, we can now apply the +1.16 kcal/mol correction from the [5s3p] → [5s4p] extension, yielding an extrapolated QCISD(T)/[5s4p2d 1f] value of +0.55 kcal/mol. Finally, applying the "QCISD(T) inadequacy" correction of 0.78 kcal/mol obtained in the [4s2p1d] basis set, our best estimate for the energy difference in the "hypothetical motionless state" is +1.33 kcal/mol, or say about 1 kcal/mol, favoring the cyclic isomer.

B. Geometries and harmonic frequencies

Geometries and harmonic frequencies were computed at the MP2/6-311G* level, as well as at the MP2/[5s3p1d] level. MP2 harmonic frequencies in the [4s2p1d] basis set used by MHB were also evaluated for the linear form, for which they did not report them. The geometries obtained are

listed in Table II, together with the available literature data. The same is done for the harmonic frequencies in Table III. For the latter, ir intensities within the double-harmonic approximation were also determined from numerical differentiation of the MP2 dipole moment.⁵⁴ Although not recommended for quantitative purposes, the intensities obtained at this level of theory should be good enough to give a qualitative picture of the relative intensities.⁵⁵

For bending frequencies of multiply bonded species, at least a [5s3p2d 1f] basis set is normally required at the MP2 level for quantitative accuracy.⁵⁶ However, such a level of theory is beyond our computational power, whereas we are primarily interested in the stretching frequencies.

The only experimental information available is the fact that a band in argon matrix at 1543.4 cm⁻¹ belongs to linear C₄,¹⁰ as well as the isotopic substitution spectrum reported in the same reference. It has already been shown,¹¹ that the isotopic substitution bands are in excellent agreement with experiment (deviations on the order of 0.2 cm⁻¹) at levels of theory ranging from UHF/4-21G to MP2/6-31G*: the levels of theory presented here form no exception.

The computed frequencies at the MP2/6-311G* and MP2/[5s3p1d] levels differ only by a relatively small amount for the linear structure, but rather significantly for the rhombic structure, consistent with the expectation that the latter will put much greater demands on the basis set for frequency evaluations. The MP2/[5s3p1d] prediction of 1551 cm⁻¹ for the experimental 1543.4 cm⁻¹ band is perhaps a fortunate result of error compensation: further improvement of basis set and electron correlation is expected to lower the frequency, whereas elimination of spin contamination would increase its value.³³ An even luckier compensation is seen with the MHB basis set, where the calculated

TABLE III. Theoretical harmonic frequencies (cm⁻¹) for the ³Σ_g⁻ and ¹A_g states of C₄. Infrared intensities (km/mol) are given in parentheses for the ir active modes. Harmonic zero point energies (ZPEs) are in kcal/mol.

Symmetry	UHF/6-31G*	MP2/6-31G**	MP2/[4s2p1d]	MP2/6-311G*	MP2/[5s3p1d]
			³ Σ _g ⁻		
Σ _g	2345	2149	2093	2128	2115
Σ _u	1740(142.3)	1586(488.3)	1544(585.0)	1562(544.9)	1551(601.8)
Σ _g	1021	951	922	935	929
Π _g	408	419	376	401	419
Π _u	210(51.2)	187(33.3)	174(27.2)	181(30.4)	185(31.6)
ZPE	9.07	8.43	8.09	8.28	8.30
			¹ A _g		
B _{1u}	1568(406.0)	1428(1262.4)	1389 ^b	1402(193.4)	1365(202.7)
A _g	1431	1298	1255 ^b	1263	1229
B _{3g}	1103	1103	1079 ^b	1077	1048
A _g	1088	934	912 ^b	924	904
B _{2u}	450(24.7)	712(184.5)	716 ^b	700(26.4)	679(25.4)
B _{3u}	350(96.4)	374(316.1)	359 ^b	355(50.5)	356(53.1)
ZPE	8.56	8.36	8.16	8.18	7.98

MP2/6-31G values are taken from Ref. 2. Our own results for the ¹A_g state are: B_{1u} 1429(187.9), A_g 1285, B_{3g} 1103, A_g 950, B_{2u} 713(27.4), B_{3u} 374(47.1). ir intensities for the Π_u mode include the twofold degeneracy.

^bTaken from MHB (Ref. 26).

value is "spot on" at 1544 cm⁻¹.

The very large intensity predicted at the MP2/6-31G* level² for the B_{1u} mode of the rhombus is in disagreement with the fairly moderate values found with other basis sets at the MP2 level. To eliminate the possibility of a misprint in Ref. 2, we reran the calculations ourselves. We then also found that the equilibrium geometry reported in Ref. 2 was not a stationary point. Our own optimum MP2/6-31G* geometry, which is also in much better agreement with the other MP2 values, is reported in a footnote to Table II. The harmonic frequencies obtained are given as a footnote to Table III. They are in near-complete agreement with the analytical gradient values given as a footnote to Table II in Ref. 2; the ir intensities, however, are much lower than those previously reported,² although they are now in good agreement with the other MP2 values.

A practical implication is that, since the ir intensity for the rhombic form is less than half that for the linear form, the two bands will only be detected at a comparable intensity if the ground state is indeed cyclic. (It should be remembered that the linear ³Σ_g⁻ state will benefit from its threefold degeneracy.)

It was already shown before^{11,12} that the only likely candidate for assignment to the B_{1u} band of the rhombus is a band at 1284 cm⁻¹.^{13,14} Application of the well-known generic scaling factors of 0.89 (Ref. 57) and 0.93,⁵⁸ respectively, to the UHF/6-31G* and MP2/6-31G* frequencies supports the assignment, as do the present higher-level results.

One might remark that upon annealing the 1284 cm⁻¹ band grows, whereas the 1544 cm⁻¹ band even decreases slightly in intensity. However, linear C₄ will easily react with C₃ to produce linear C₇,³⁰ which is not so evident for the cyclic form. Furthermore, the two forms do not readily interconvert, which means that on kinetic grounds, linear C₄ will be depleted much faster than cyclic C₄, although both will continue to be formed from the smaller components of the trapped vapor. Finally, the additional rotational degree of freedom of the cyclic will by itself displace the isomerization constant in its favor by a factor \sqrt{T} , until the linear form starts benefiting from its low bending frequencies at somewhat higher temperatures (> 50–100 K). All this serves mainly to illustrate that the 1284 cm⁻¹ assignment cannot

necessarily be ruled out on the basis of thermal annealing behavior.

Detection of the band and recording of either a rotational fine structure or an isotopic substitution spectrum should normally give fairly conclusive evidence whether the linear and cyclic isomers coexist or not. In order to facilitate the latter, we have given in Table IV the computed isotopic substitution spectrum at various levels of theory. Evidently, the computed values converge quite rapidly with increasing theoretical level; the MP2/6-311G* and MP2/[5s3p1d] values are even indistinguishable. Because the force constants will not be described as well as for the linear stretching force constants, the agreement with experiment may be somewhat worse than in the latter case, but the spectrum's appearance is itself characteristic enough. The rotational fine structure for an asymmetric top is of course easily distinguished from that of a linear molecule.

Given the difference in oscillator strengths and the additional degeneracy entropy of the linear form, coexistence at these low temperatures normally implies that the rhombus is very slightly below the linear form, as predicted by the present calculations.

Zero point energies (ZPEs) within the RRHO (rigid rotor-harmonic oscillator) approximation may be derived from the computed frequencies (the HF/6-31G* and MP2/6-31G* should be scaled by factors of 0.89 and 0.93, respectively). Their effect on the computed ΔE is very small (0.1–0.3 kcal/mol). All levels of theory except MP2/[4s2p1d] predict that it favors the cyclic structure; however, given the smallness of the effects, no definitive conclusion about that can be made without taking anharmonic corrections into account. Enlarging the basis set will normally lower the computed frequencies for the cyclic a little more than for the linear; on the other hand, the degenerate bending modes of the linear may be significantly affected too, which works in the opposite direction. Our main conclusion regarding the ZPE effect is that its neglect should be negligible compared to the other errors inherent in the calculations.

IV. HEAT OF FORMATION OF C₄

There are two generally quoted literature sources for the heat of formation of C₄: the JANAF tables,⁵⁹ where a value

TABLE IV. Computed isotopic substitution spectrum for the hypothetical 1284 cm⁻¹ band or rhombic C₄.^a

Isotopomer	Wt.	HF/4-21G	HF/6-31G*	MP2/6-31G*	MP2/6-311G*	MP2/[5s3p1d]
12-12-12-12	1	1284.0	1284.0	1284.0	1284.0	1284.0
12-12-12-13	2	1271.8	1271.9	1272.1	1272.1	1272.1
12-12-13-12	2	1272.5	1272.8	1272.7	1272.7	1272.7
12-12-13-13	4	1260.2	1260.6	1260.8	1260.7	1260.8
12-13-12-13	1	1259.0	1259.0	1259.0	1259.0	1259.0
13-12-13-12	1	1259.0	1259.0	1259.0	1259.0	1259.0
12-13-13-13	2	1247.4	1247.6	1247.6	1247.6	1247.6
13-12-13-13	2	1246.5	1246.7	1246.9	1246.8	1246.8
13-13-13-13	1	1233.5	1233.5	1233.5	1233.5	1233.5

^aThe first atom is situated along the largest diagonal of the rhombus. Subsequent atoms are numbered either clockwise or counterclockwise (the two possibilities are equivalent by symmetry).

of 232 kcal/mol is given, and the classic note of Drowart *et al.*,⁶⁰ who found (using the Knudsen effusion technique) a second-law value of 229.5 ± 7.1 kcal/mol and third-law values (using two different partition functions) of 240.5 ± 5.8 and 237.5 ± 5.8 kcal/mol, respectively. These values were based on a heat of formation for C(g) of 169.58 kcal/mol, which is listed in the JANAF tables as 169.98 kcal/mol. Hence, another 1.6 kcal/mol should be added to bring the values for C₄ on the same scale as our theoretical determination.

The latter follows the standard G1 recipe as outlined in Ref. 37. Atomic energies involved in the calculation may be found in Table V. Taking all the customary terms into account, we find a ΣD_e of 437.9 and a ΣD_0 of 430.3 kcal/mol, which means a heat of formation of 249.6 kcal/mol. This value is normally claimed to be accurate to ± 2 kcal/mol. We will not claim this kind of accuracy for such a “difficult” molecule; however, the 232 and 229.5 kcal/mol values are clearly outside the expected error range. Using PMP4 instead of MP4 energies for the additivity calculation lowers the computed dissociation energies by 0.58 kcal/mol (and of course increases the heat of formation by the same amount).

The free energy functions $-[G(T) - H(0)]/T$ used by Drowart *et al.* in their third-law extrapolation are actually semiempirical estimates by Pitzer and Clementi.⁶¹ Seeing these as a potential error source, we have re-evaluated the free energy functions—within the RRHO (rigid rotor-harmonic oscillator) approximation—ourselves with the available *ab initio* data. At the temperatures of interest, anharmonic, centrifugal distortion, and rotation-vibration coupling effects may be of some importance; however, even our crude RRHO functions should be much more reliable than the Pitzer–Clementi “thumbnail estimates.”

Details of the RRHO calculation are as follows. Harmonic frequencies and rotational constants were taken to be unscaled MP2/[5s3p1d] values, with all isotopes ¹²C throughout. The electronic partition function was assumed to be factorizable, and set up separately for the linear and cyclic forms. The necessary transition energies were MRD-CI/DZP values taken from Ref. 35, this data set being the most complete. The isomerization energy at absolute zero was taken to be +1.0 kcal/mol, and the internal partition function thus constructed from those for the linear and cyclic isomers. Finally, the translational contribution was added in, with the molecular weight computed from the natural isotopic abundances.

Computed free energy functions at 2000, 2500, and 3000 K, respectively, are 77.09, 81.19, and 84.66 e.u., in excess of 2 e.u. above the Pitzer–Clementi values. The final values are quite close to those for the linear isomer by itself, illustrating that the latter will dominate at higher temperatures even though it is not the ground state, strictly speaking. Correcting the Drowart *et al.* values for the new free energy functions, we find an average heat of formation of 246.7 kcal/mol. Correcting for the different reference values for the heat of formation of the C(g) atom, this even increases to 248.3 kcal/mol, in good agreement with our theoretical determination. (Assuming the linear and cyclic forms to be isoenergetic yields free energy functions of 77.53, 81.55, and 84.96 e.u.

TABLE V. Atomic energies (hartree) used in dissociation energy calculations.

Basis	MP4	PMP4(1)	QCISD(T)
6-311G*	− 37.764 302	− 37.764 797	− 37.766 695
6-311 + G*	− 37.765 199	− 37.765 808	
6-311G(2df)	− 37.774 830	− 37.775 441	
[5s3p1d]	− 37.767 208	− 37.767 761	− 37.769 755
[5s4p1d]	− 37.769 366	− 37.769 913	
[5s3p2d 1f]	− 37.777 538	− 37.778 186	

at 2000, 2500, and 3000 K, respectively. These values would imply an additional 0.9 kcal/mol increase in the third-law heat of formation.)

Quite surprisingly, redoing the entire G1 procedure with a [5s3p] valence set substituted for the 6-311G one has a rather significant effect on the results. The correction terms have been evaluated according to the same recipe as the ones in the original G1 publication, and are in excellent agreement with them

$$\Delta E_{\text{HLC}} = -0.19n_{\alpha} - 5.96n_{\beta} \text{ mhartrees}, \quad (1)$$

where n_{α} and n_{β} represent the number of spin-up and spin-down electrons, as customary. At the G1/[5s3p2d 1f] level, we arrive at $\Sigma D_e = 434.3$ and $\Sigma D_0 = 426.7$ kcal/mol, or a heat of formation of 253.3 kcal/mol, still in marginal agreement with the revised “experimental” value. At the G1/6-311G(2df) level (i.e., ignoring the diffuse functions) we find a $\Sigma D_e = 436.9$ kcal/mol, which explains part but not all of the discrepancy between the two basis set families. Taking the [5s3p1d] → [5s4p1d] extension into account too, however, we arrive at a value in good agreement with both the experimental and G1/6-311 + G(2df) values, namely $\Sigma D_e = 438.1$, $\Sigma D_0 = 430.5$, and $\Delta H_0^{\circ} = 249.4$ kcal/mol. As a final note, using PMP4 instead of MP4 in the additivity calculations leads to ΣD_e lowerings of 0.24, 0.22, and 0.29 kcal/mol for the G1/[5s3p2d 1f], G1/[5s4p2d 1f], and G1/6-311G(2df) results, respectively.

In assigning an approximate error bar for the computed heats of formation we should consider a few further possible error sources. These include inadequacy of the electron correlation treatment, which may have an effect on the order of a few kcal/mol at most, and nonadditivity of basis set and electron correlation effects. To assess the possible magnitude of these, we redid our previous calculation of the heat of formation of C₃ (Ref. 50) [where the additivity was assumed only at the CCD(ST) level instead of the MP4 level] using conventional G1 theory and found an error of only 0.5 kcal/mol. A safe error estimate for our theoretical value is then something like ± 4 kcal/mol.

All this appears to indicate that the heats of formation hitherto assumed for C₄ are much too low, that the Drowart *et al.* third-law value might be close to the actual value, and that an experimental redetermination and/or an *ab initio* study at a higher level are indicated.

Note added

Just before submitting the present paper, we received a preprint from V. Parasuk and J. Almlöf,⁶² where partial-

valence CASSCF (complete active space SCF⁶³) and partial and full-valence MRCI⁶⁴ results are reported for C₄. With the MHB basis set (but the redundant *s* function eliminated from the *d* shell), these authors found a ΔE of -2.7 kcal/mol at the MRCI level. This indicates that a multireference treatment will normally not have a devastating effect on the present results. At their best level of theory (which was MRCI in a [4s4p2d1f] atomic natural orbital (ANO)⁶⁵ basis set, with all configurations whose coefficients exceed 0.05 in a 10/10 CASSCF being included in the reference set), these authors found the linear form to be 4.5 kcal/mol lower than the cyclic form. However, direct MP2 calculations with basis sets up to [6s5p4d2f] indicate that further basis set expansion will favor the cyclic, leading these authors to conclude that the two forms will be nearly isoenergetic. This latter conclusion is in agreement with that reached in the present paper.

Dr. Jan Almlöf kindly suggested investigating the effect of basis set superposition error (BSSE), as it tends to artificially favor the cyclic form.⁶⁶ Whereas the last word on the validity of the counterpoise (CP) procedure⁶⁷ has not nearly been said,⁶⁸ we have computed the CP corrections at the PMP4 level using the site-site function counterpoise method⁶⁹ (The extension of the CP to interactions involving more than two subsystems, such as ΣD_e values for polyatomics, is not unique.) At the PMP4/[5s3p2d1f] level, the CP correction favors the linear structure by 0.77 kcal/mol, compared to 2.57 and 2.24 kcal/mol at the PMP4/[5s4p1d] and PMP4/[5s3p1d] levels, respectively. Applying the full CP correction would consequently lead to a nearly vanishing ΔE . On the other hand, the fully CP corrected ΔE increases by about 1 kcal/mol each for the two basis set extensions considered. Extrapolating this trend for further basis set extensions suggests that the cyclic form would indeed be slightly below the linear form in the infinite-basis limit. We agree with Dr. Almlöf though, that it is a bit pointless to argue about the ground state on the basis of currently achievable theoretical results alone, and hope that some of the results presented in this paper may aid experimentalists to settle the issue by indirect evidence.

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¹ W. Weltner, Jr. and R. J. Van Zee, *Chem. Rev.* **89**, 1713 (1989).

² D. Michalska, H. Chojnacki, B. A. Hess, Jr., and L. J. Schaad, *Chem. Phys. Lett.* **141**, 376 (1987).

³ D. E. Bernholdt, D. H. Magers, and R. J. Bartlett, *J. Chem. Phys.* **89**, 3612 (1988).

⁴ J. M. L. Martin, J. P. François, and R. Gijbels, *J. Chem. Phys.* **90**, 3403 (1989).

⁵ P. Botschwina and P. Sebal, *Chem. Phys. Lett.* **160**, 485 (1989).

⁶ L. Adamowicz and J. Kurtz, *Chem. Phys. Lett.* **162**, 342 (1989).

⁷ M. Vala, T. M. Chandrasekhar, J. Szczepanski, R. J. Van Zee, and W. Weltner, Jr., *J. Chem. Phys.* **90**, 595 (1989).

⁸ P. F. Bernath, K. H. Hinkle, and J. J. Keady, *Science* **244**, 562 (1989).

⁹ J. R. Heath, A. L. Cooks, M. H. W. Gruebele, C. A. Schmuttenmaer, and R. J. Saykally, *Science* **244**, 564 (1989).

¹⁰ L. N. Shen and W. R. M. Graham, *J. Chem. Phys.* **91**, 5115 (1989).

¹¹ J. M. L. Martin, J. P. François, and R. Gijbels, *J. Chem. Phys.* **93**, 8850 (1990).

¹² J. M. L. Martin, J. P. François, and R. Gijbels, *J. Comp. Chem.*, **11**, (in press).

¹³ K. R. Thompson, R. L. DeKock, and W. Weltner, Jr., *J. Am. Chem. Soc.* **93**, 4688 (1971).

¹⁴ W. Krätschmer and K. Nachtigall, in *Polycyclic Aromatic Hydrocarbons and Astrophysics*, edited by A. Léger et al. (Reidel, Dordrecht, 1987), p. 75.

¹⁵ J. R. Heath, R. A. Sheeks, A. L. Cooks, and R. J. Saykally, *Science* **249**, 895 (1990); J. R. Heath and R. J. Saykally, *J. Chem. Phys.* **93**, 8392 (1990); J. R. Heath and R. J. Saykally, *J. Chem. Phys.* (in press).

¹⁶ M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.* **99**, 4899 (1977).

¹⁷ Z. Slanina and R. Zahradnik, *J. Phys. Chem.* **81**, 2252 (1977).

¹⁸ R. A. Whiteside, R. Krishnan, D. J. DeFrees, J. A. Pople, and P. von Ragué Schleyer, *Chem. Phys. Lett.* **78**, 538 (1981).

¹⁹ R. Krishnan and J. A. Pople, *Int. J. Quantum Chem.* **14**, 91 (1978).

²⁰ W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.* **56**, 2257 (1972).

²¹ P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta* **28**, 213 (1973); *Chem. Phys. Lett.* **16**, 217 (1972).

²² J. P. Ritchie, H. F. King, and W. S. Young, *J. Chem. Phys.* **85**, 5175 (1986).

²³ S. R. Langhoff and E. R. Davidson, *Int. J. Quantum Chem.* **8**, 61 (1974).

²⁴ S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965).

²⁵ T. H. Dunning, Jr., *Chem. Phys.* **53**, 2823 (1970).

²⁶ D. H. Magers, R. J. Harrison, and R. J. Bartlett, *J. Chem. Phys.* **84**, 3284 (1986).

²⁷ R. Krishnan, M. J. Frisch, and J. A. Pople, *J. Chem. Phys.* **72**, 4244 (1980).

²⁸ R. J. Bartlett, *J. Phys. Chem.* **93**, 1697 (1989).

²⁹ Y. S. Lee, S. A. Kucharski, and R. J. Bartlett, *J. Chem. Phys.* **81**, 5906 (1984).

³⁰ K. Raghavachari and J. S. Binkley, *J. Chem. Phys.* **87**, 2191 (1987).

³¹ K. Raghavachari, *J. Chem. Phys.* **82**, 4607 (1985).

³² H. B. Schlegel, *J. Phys. Chem.* **92**, 3075 (1988).

³³ J. M. L. Martin, J. P. François, and R. Gijbels, *Chem. Phys. Lett.* **166**, 238 (1989).

³⁴ J. M. L. Martin, M. Sc. thesis, University of Antwerp, 1987.

³⁵ R. J. Buenker and S. D. Peyerimhoff, *Theor. Chim. Acta* **35**, 33 (1974); R. J. Buenker, S. D. Peyerimhoff, and W. Butscher, *Mol. Phys.* **35**, 771 (1978); R. J. Buenker and R. A. Phillips, *J. Mol. Struct. (THEOCHEM)* **123**, 291 (1985).

³⁶ G. Pacchioni and J. Koutecký, *J. Chem. Phys.* **88**, 1066 (1988).

³⁷ J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, and L. A. Curtiss, *J. Chem. Phys.* **90**, 5622 (1989).

³⁸ M. J. Frisch, M. Head-Gordon, H. B. Schlegel, K. Raghavachari, J. S. Binkley, C. Gonzalez, D. J. DeFrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, E. M. Fluder, S. Topiol, and J. A. Pople, GAUSSIAN 88 release C (Gaussian, Pittsburgh, 1989).

³⁹ M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohlfing, L. R. Kahn, D. J. DeFrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fluder, and J. A. Pople, GAUSSIAN 86 release C (Carnegie-Mellon University, Pittsburgh, 1987).

⁴⁰ J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, *Int. J. Quantum Chem. Symp.* **13**, 225 (1979).

⁴¹ N. C. Handy and H. F. Schaefer III, *J. Chem. Phys.* **81**, 5031 (1984); N. C. Handy, R. D. Amos, J. F. Gaw, J. E. Rice, E. D. Simandiras, T. J. Lee, R. J. Harrison, W. D. Laidig, G. B. Fitzgerald, and R. J. Bartlett, in *Geometrical Derivatives of Energy Surfaces and Molecular Properties*, NATO ASI Series, edited by P. Jørgensen and J. Simons (Reidel, Dordrecht, 1986), p. 179.

⁴² J. A. Pople, M. Head-Gordon, and K. Raghavachari, *J. Chem. Phys.* **87**, 5968 (1987).

⁴³ K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).

- ⁴⁴T. J. Lee, A. P. Rendell, and P. R. Taylor, *J. Phys. Chem.* **94**, 5463 (1990).
- ⁴⁵H. B. Schlegel, *J. Chem. Phys.* **84**, 4530 (1986).
- ⁴⁶R. J. Bartlett, *Ann. Rev. Phys. Chem.* **32**, 359 (1981), and references therein.
- ⁴⁷M. Urban, J. Noga, S. J. Cole, and R. J. Bartlett, *J. Chem. Phys.* **83**, 4041 (1985). The acronym denotes CCSD with a quasiperturbative treatment of the triples based on the double excitation amplitudes only, as opposed to CCSD(T) where it is based upon both singles and doubles amplitudes. The two methods differ at fifth order in perturbation theory.
- ⁴⁸R. S. Grev and H. F. Schaefer III, *J. Chem. Phys.* **91**, 7305 (1989).
- ⁴⁹R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.* **72**, 650 (1980).
- ⁵⁰J. M. L. Martin, J. P. François, and R. Gijbels, *J. Chem. Phys.* **93**, 5037 (1990).
- ⁵¹T. Clark, J. Chandrasekar, G. W. Spitznagel, and P. Von Ragué Schleyer, *J. Comp. Chem.* **4**, 294 (1983).
- ⁵²G. E. Scuseria and H. F. Schaefer III, *J. Chem. Phys.* **90**, 3629 (1989).
- ⁵³M. J. Frisch, J. A. Pople, and J. S. Binkley, *J. Chem. Phys.* **80**, 3265 (1984).
- ⁵⁴Y. Yamaguchi, M. Frisch, J. Gaw, H. F. Schaefer III, and J. S. Binkley, *J. Chem. Phys.* **84**, 2262 (1986).
- ⁵⁵B. A. Hess, Jr., L. J. Schaad, P. Čársky, and R. Zahradník, *Chem. Rev.* **86**, 709 (1986).
- ⁵⁶E. D. Simandiras, J. E. Rice, T. J. Lee, R. D. Amos, and N. C. Handy, *J. Chem. Phys.* **88**, 3187 (1988).
- ⁵⁷J. A. Pople, H. B. Schlegel, R. Krishnan, D. J. DeFrees, J. S. Binkley, M. J. Frisch, R. A. Whiteside, R. F. Hout, and W. J. Hehre, *Int. J. Quantum Chem. Symp.* **15**, 269 (1981).
- ⁵⁸R. F. Hout, Jr., B. A. Levi, and W. J. Hehre, *J. Comp. Chem.* **3**, 234 (1982).
- ⁵⁹M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF thermochemical tables*, 3rd ed. (American Chemical Society and American Institute of Physics for the National Bureau of Standards, New York, 1985).
- ⁶⁰J. Drowart, R. P. Burns, G. DeMaria, and M. G. Inghram, *J. Chem. Phys.* **31**, 1131 (1959).
- ⁶¹K. S. Pitzer and E. Clementi, *J. Am. Chem. Soc.* **81**, 4477 (1959).
- ⁶²V. Parasuk and J. Almlöf, *J. Chem. Phys.* (in press).
- ⁶³B. O. Roos, *Adv. Chem. Phys.* **69**, 399 (1987).
- ⁶⁴C. W. Bauschlicher, Jr., S. R. Langhoff, and P. R. Taylor, *Adv. Chem. Phys.* **77**, 103 (1990).
- ⁶⁵J. Almlöf and P. R. Taylor, *J. Chem. Phys.* **86**, 4070 (1987).
- ⁶⁶V. Parasuk, J. Almlöf, and B. DeLeeuw, *Chem. Phys. Lett.* **176**, 1 (1991).
- ⁶⁷S. F. Boys and F. Bernardi, *Mol. Phys.* **19**, 553 (1970).
- ⁶⁸J. M. L. Martin, J. P. François, and R. Gijbels, *Theor. Chim. Acta* **76**, 195 (1989), and references therein.
- ⁶⁹B. H. Wells and S. Wilson, *Chem. Phys. Lett.* **101**, 429 (1983).