The Bismuth Tetramer Bi_4: The v_3 Key to Experimental Observation

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The Bismuth Tetramer Bi_4: The ν_3 Key to Experimental Observation†

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The spectroscopic identification of Bi_4 has been very elusive. Two constitutional Bi_4 isomers of T_d and C_{2v} symmetry are investigated and each is found to be a local energetic minimum. The optimized geometries and vibrational frequencies of these two isomers are obtained at the CCSD(T)/cc-pVQZ-PP level of theory, utilizing the Stoll, Metz, and Dolg 60-electron effective core potential. The fundamental frequencies of the T_d isomer are obtained at the same level of theory. The focal point analysis method, from a maximum basis set of cc-pV5Z-PP, and proceeding to a maximum correlation method of CCSDT(Q), was employed to determine the dissociation energy of Bi_4 (T_d) into two Bi_2 and the adiabatic energy difference between the C_{2v} and T_d isomers of Bi_4. These quantities are predicted to be +65 kcal mol^{-1} and +39 kcal mol^{-1}, respectively. Two electron vertical excitation energies between the T_d and C_{2v} electronic configurations are computed to be 156 kcal mol^{-1} for the T_d isomer and 9 kcal mol^{-1} for the C_{2v} isomer. The most probable approach to laboratory spectroscopic identification of Bi_4 is via an infrared spectrum. The predicted fundamentals (cm^{-1}) with IR intensities in parentheses (km mol^{-1}) are 94(0), 123(0.23), and 167(0) for the T_d isomer. The moderate IR intensity for the only allowed fundamental may explain why Bi_4 has yet to be observed. Through natural bond orbital analysis, the C_{2v} isomer of Bi_4 was discovered to exhibit "long-bonding" between the furthest apart 'wing' atoms. This long-bonding is postulated to be facilitated by the σ-bonding orbital between the 'spine' atoms of the C_{2v} isomer.

1 Introduction

Given the remarkable stability of P_4, it is not unreasonable to search for its heavier valence isoelectronic species. Despite many attempts, it is unclear whether the Bi_4 molecule has been positively identified in the laboratory, apart from mass spectrometry in several studies,[1–5] most recently those of Duncan and coworkers.[6,7] As of yet, no vibronic spectra have been unambiguously assigned to this molecule, though many have tried.[8–12] Although Bi_4 has proven evasive to spectroscopists, it has been explored by theoretical chemists using several varieties of density functional theory (DFT). Various characteristics of Bi_4 have been studied, including its electronic structure,[13–16] electron affinity,[14,16–18] ionization potential,[14,16,18], and binding energy,[14,19]. The preferred geometry[13,14,16,18–21] and harmonic vibrational frequencies[14,19] of Bi_4 have been computed mostly by DFT studies, with one study[13] utilizing dynamical correlation methods. Though DFT and static correlation methods have been fruitful in many endeavors such as pnictogen materials studies,[22,23] these methods are not the highest level of theory that may be utilized, and high precision is of the utmost importance for this system.

Several spectroscopic studies[8–12] initially claimed to have identified three vibronic emission bands of Bi_4. Arrington and Morse[24] later (2008) observed these same emission bands but identified the source as Bi_3 via time-of-flight mass spectrometry. An excellent *ab initio* analysis of the electronic structure of Bi_4 at the MRCISD/CASSCF level of theory was provided by Zhang and Balasubramanian as early as 1992.[13] In the latter study, the authors give further evidence that these emission bands should not be assigned to Bi_4 on the grounds that only one of the low energy Bi_4 electronic excitations is formally dipole allowed, and its expected excitation energy is qualitatively different from the excitations observed. Additionally, Wakabayashi et al. analyzed small bismuth clusters using laser induced fluorescence spectroscopy and their results also support the reassignment of the supposed Bi_4 emission bands to Bi_3.[25,26]

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Several theoretical studies have explored the energetically low-lying constitutional isomers of Bi_4 and their corresponding harmonic vibrational frequencies, although the highest level of theory used in these studies was MRCISD with a triple zeta basis set. From a Lewis-bonding perspective,[27] one would expect that the lowest energy isomer would be one that has three bonds per bismuth to find pairs for its three unpaired valence electrons. Jia et al. noted that due to the relativistic contraction of the bismuth 6s orbital,[14] covalent bonding in Bi_n species will be dominated by the 6p orbitals. While the Lewis-bonding perspective yields one constitutional isomer of Bi_4, other energetic local minima isomers are theoretically possible.

Lauher[28] lists four possible geometric isomers of metal cluster tetramers labeled as tetrahedral (T_d), butterfly (C_{2v} and D_{2h}), and square planar (D_{4h}). Yuan et al. predicted the three lowest energy isomers of Bi_4, utilizing the BPW functional with a relativisitic effective core potential (RECP) and a double numeric plus d polarization functions (DN+d) basis set, to be, T_d, C_{2v} (+27.4 kcal mol^{-1}), and D_{4h}(+39.9 kcal mol^{-1}).[18] Akola and co-workers mention only the T_d and C_{2v} structures as low energy isomers in their computations using the PBE functional with an RECP and a plane-wave basis ,[19] shedding some doubt on the existence of the square planar isomer. Several studies[29–32] have shown that the C_{2v} isomer can exist for P_4 analogues if a ligand is inserted into a bond, thus giving experimental validation for the existence of this isomer in group 5 tetramers. Gausa et al. found the lowest energy isomer of the Bi_4^- anion to be the C_{2v} structure,[16] begging the question of why the T_d isomer is not a minimum for the anion. Jia et al. determined the lowest energy isomer of neutral Bi_4 to be the T_d structure through PBE/DN+d with RECP computations. However, they computed the D_{2d} structure of anionic Bi_4^- to be the lowest in energy, again not finding an anionic T_d local minimum.[14] Considering the longstanding misassignment of spectra previously mentioned, no isomers of Bi_4 have been spectroscopically confirmed.

Theoretical treatment of bismuth clusters comes with its own set of challenges. The considerable number of electrons to be modeled, along with the presence of relativistic effects within the immense core has resulted in many low level theoretical treatments. One method of solving both of these problems has been the application of effective core potentials (ECPs).[33] This computational tool accounts for relativistic core effects while allowing for high-level correlation treatments, such as coupled-cluster (CC) theory, of the valence electrons. In the case of bismuth, small core ECPs reduce the number of explicitly treated electrons to those occupying the valence 5s, 5p, 5d, 6s, and 6p-orbitals. The Bi_4 molecule will thus be analyzed with the aid of ECPs in this study.

Optimized equilibrium geometries and harmonic vibrational frequencies for Bi_4 isomers of T_d and C_{2v} symmetry were computed in this study. These two isomers were found to be the only local minima of those mentioned by Lauher.[28] Additionally, the energy difference between these isomers and the dissociation energy of Bi_4 (T_d) into two Bi_2 molecules were obtained, and Natural Bond Orbital[34] (NBO) analysis was performed on the T_d and C_{2v} isomers.

2 Theoretical Methods

The equilibrium geometries were obtained by utilizing Peterson's[35] correlation consistent quadruple-ζ basis set designed for use with relativistic psuedopotentials[33] (cc-pVQZ-PP). The small core psuedopotentials used in this work were developed by Dolg and coworkers[33] and encompass all electrons that are not present in the 5s, 5p, 5d, 6s, and 6p orbitals of bismuth. This ECP60MDF encompasses 60 electrons per bismuth and allows for treatment of the remaining 23 electrons per bismuth with Hartree-Fock and post Hartree-Fock methods. We then selected 18 of the electrons per bismuth to be frozen as core orbitals so that only the 5 valence electrons per bismuth were treated with correlation methods. Coupled cluster theory with full single, double, and perturbative treatment of triple excitations[36,37] [CCSD(T)] was utilized in the geometry optimizations with the CFOUR 2.0[38] (henceforth CFOUR) suite of electronic structure codes. The T_d and C_{2v} isomer geometry optimizations had convergence criteria for the RMS energy gradient of 10^{-10}. MOLPRO 2010[39] was utilized to check for multireference character in the wavefunction space of each isomer through its T_1[40] and D_1[41] diagnostics. NBO[34] analysis was performed on both isomers utilizing the Q-Chem 5.0[42] quantum chemistry software package interfaced with NBO 6.0[43] augmented by Natural Resonance Theory (NRT).[44]

Harmonic vibrational frequencies were obtained using a 5-point finite difference method also utilizing CFOUR at the CCSD(T)/cc-pVQZ-PP level of theory as well, and with the same convergence criteria as the geometry optimizations. After the harmonic frequencies were obtained they were inspected to ensure that no imaginary vibrational modes were present and that each optimized geometry represented a genuine minimum on the potential energy surface (PES). Full cubic and semidiagonal quartic anharmonic corrections to the harmonic vibrational frequencies were computed using second order vibrational perturbation theory (VPT2)[45,46] through finite differences, as implemented within CFOUR and at the same level of theory as that for the harmonic vibrational frequencies.

Focal point analysis[47–50] was employed in determining the dissociation energy of $Bi_4 \rightarrow 2Bi_2$ and the relative energy between the T_d and C_{2v} isomers. The single point energies, computed in the range of cc-pVnZ-PP ($n = D,T,Q,5$), and with a reference geometry optimized at the CCSD(T)/cc-pVQZ-PP level of theory, were utilized to extrapolate to the complete basis set (CBS) limit. Correlation energy methods up to coupled cluster single, double, triple, and quadruple excitations (CCSDTQ) were utilized. Extrapolation to the CBS limit for the restricted Hartree–Fock energies and correlation energies were accomplished by three-point[51] and two-point[52] extrapolation schemes, respectively, with the following functions.

$$E_{\mathrm{HF}}(X) = E_{HF}^{\infty} + ae^{-bX} \quad (1)$$

$$E_{corr}(X) = E_{corr}^{\infty} + X^{-3} \quad (2)$$

The determination of the correlation energy due to full triples and perturbative quadruples excitation for basis set sizes up to the extrapolated CBS limit was accomplished by assuming additivity from the perturbative triples to the full triples and full triples correlation energy to the perturbative quadruples energy computed with the cc-pVTZ-PP basis set and utilizing this same energy difference for all larger basis set sizes.

The CCSD(T) and CCSDT(Q) computations were both run in CFOUR [38] utilizing the ECC [38] and NCC [53–55] modules, respectively. Diagonal Born–Oppenheimer corrections [56,57] (DBOCs) and relativistic corrections were carried out at the HF/cc-pVTZ-PP and CCSD(T)/cc-pVTZ-PP levels of theory, respectively. The scalar relativistic corrections were computed through second order perturbation theory with mass-velocity and Darwin terms (MVD2). [58,59]

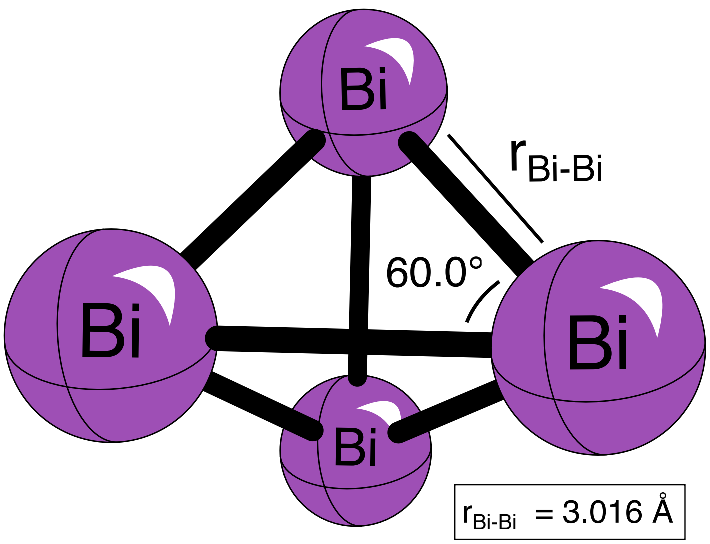


Fig. 1 The equilibrium geometry of the T_d isomer of Bi_4 predicted at the CCSD(T)/cc-pVQZ-PP level of theory.

3 Results and Discussion

3.1 Geometries

3.1.1 T_d Structure

The T_d is the most thoroughly studied of the two isomers of Bi_4 presented in this paper. The T_d isomer has a valence electron configuration of $1a_1^2 1b_1^2 2a_1^2 1b_2^2 3a_1^2 2b_1^2 4a_1^2 2b_2^2 5a_1^2 1a_2^2$. Numerous studies [13,14,18–20,60] report an equilibrium geometry for this isomer at low levels of theory, and these structures will be compared to the geometries predicted in this research. When examining the methods used among previous studies it may be seen that the geometries computed in this research were obtained at a more rigorous level than any of its predecessors. Many of the prior studies utilize plane-wave basis sets and DFT to recover the correlation energy and these methods are less reliable than the methods used in this work. Balasubramanian and Zhang [13] used multireference methods (CASSCF and MRCISD) to analyze excited states of the T_d isomer, and so the T_1 and D_1 diagnostics for this system were computed in the present research, and found to be 0.015 and 0.027, respectively. The value for the D_1 diagnostic is in an intermediary range [61] indicating that there may be some multireference character to the T_d isomer. Optimizing the geometry and computing the vibrational frequencies with a high level of dynamic correlation, however, should recover multireference character. This effect is supported by the focal point energies discussed in the Energetics section of this paper, as there is fairly good convergence of the electron correlation methods. So while Balasubramanian and Zhang used multireference methods, we are confident that our system geometry is well described by single reference CCSD(T). No previous studies have treated Bi_4 with coupled cluster methods and so this work represents the most rigorous treatment that Bi_4 has received thus far.

A serendipitous aspect of optimizing the T_d isomer is that due to the high amount of symmetry present, the only coordinate to be optimized is the Bi-Bi bond distance. This Bi-Bi bond distance is visualized in Figure 1 as r_{Bi-Bi}. The (most reliable) optimized r_{Bi-Bi} bond length was computed to be 3.016 Å in this study. When this bond length is compared to the bond lengths computed in prior studies [13,14,18–20] it may be seen that the r_{Bi-Bi} predicted in this research is among the smallest. Gao et al. [20] compute a value of 3.02 Å, matching the value computed in this study within provided precision. It should be noted that Gao et al. utilized the PW91 functional with plane wave basis sets, so it is among the lower levels of theory discussed here. Zhang and Balasubramanian [13] computed the r_{Bi-Bi} value with the highest deviation from our study, that deviation being 0.1 Å. They utilized MRCISD with a triple zeta equivalent basis set including d polarization functions and a relativistic ECP that spanned only 5 valence electrons per bismuth (those contained in the 6*s* and 6*p*-orbitals). Bond lengths can affect many properties of a molecule including the frequencies reported in this work and this effect will be discussed later.

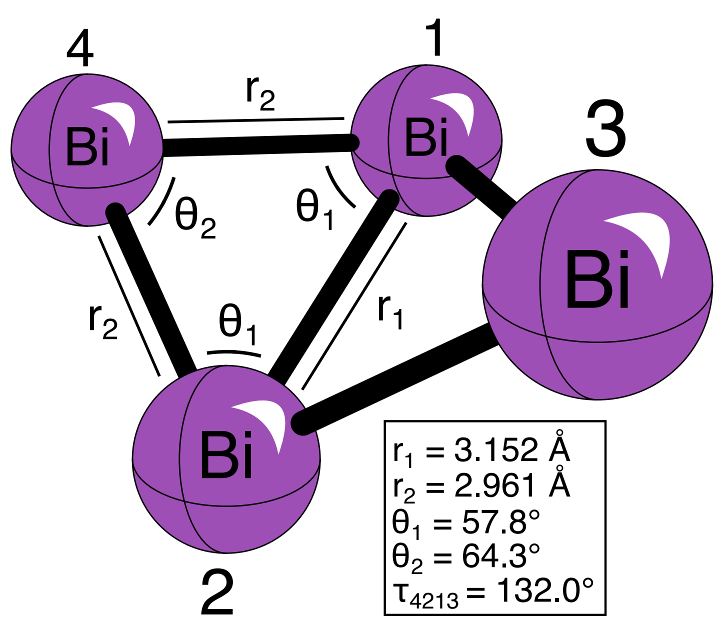


Fig. 2 The equilibrium geometry of the C_{2v} isomer of Bi_4 predicted at the CCSD(T)/cc-pVQZ-PP level of theory.

3.1.2 C_{2v} Structure

When discussing the C_{2v} isomer, two terms will be used to describe pairs of symmetric atoms. These terms are the 'spine' and

Table 1 Harmonic and anharmonic vibrational frequencies for the T_d Bi_4 (in cm^{-1}) structure at the CCSD(T)/cc-pVQZ-PP level of theory. The v_3 harmonic IR intensity is reported in parentheses (in km mol^{-1})

Vibrational Mode	Harmonic Frequency	Fundamental Frequency
$v_1(a_1)$	168(0)	167
$v_2(e)$	95(0)	94
$v_3(t_2)$	123(0.23)	123

Table 2 Harmonic vibrational frequencies for the C_{2v} Bi_4 (in cm^{-1}) structure at the CCSD(T)/cc-pVQZ-PP level of theory. Harmonic IR intensities are reported in parentheses (in km mol^{-1})

Vibrational Mode	Harmonic Frequency
$v_1(a_1)$	148(0.04)
$v_2(a_1)$	84(0.02)
$v_3(a_1)$	49(0.01)
$v_4(a_2)$	100(0)
$v_5(b_1)$	132(4.04)
$v_6(b_2)$	108(0.02)

'wing' atoms which will henceforth refer to atoms 1 and 2, and atoms 3 and 4, respectively, of Figure 2.

While performing optimizations on the C_{2v} isomer it was necessary to impose a specific electronic state to keep the geometry from relaxing to the T_d isomer, even though the C_{2v} is indeed a local minimum. It appears that the T_d and C_{2v} isomers lie on two different potential energy surfaces and while it was not rigorously studied in this work, the interaction between these surfaces (especially in geometries intermediate to the T_d and C_{2v} isomers) would be a fascinating avenue for future study. The valence electronic configuration of the C_{2v} structure is $1a_1^2 1b_1^2 1b_2^2 2a_1^2 3a_1^2 1a_2^2 2b_1^2 4a_1^2 2b_2^2 3b_1^2$.

The C_{2v} isomer has been studied far less in previous research than the T_d isomer. A straightforward explanation for this discrepancy is that the T_d isomer is the lowest energy isomer, and when Bi_4 is generated the T_d isomer is expected to be the most abundant of the two. Additionally, the C_{2v} isomer is on a separate electronic PES from the T_d isomer. The C_{2v} structure was found to exhibit strong multireference character with a T_1 diagnostic of 0.030 and a D_1 diagnostic of 0.106. In light of these obstacles, only one other study[19] has reported a geometry for the neutral C_{2v} isomer.

As with the T_d isomer the bond lengths reported by this work for the C_{2v} constiutional isomer are shorter than those of the previous work.[19] Akola et al. (henceforth Akola) utilized the PBE functional with a plane wave basis. Akola report an r_1 of 3.19 Å and an r_2 of 2.98 Å, both deviating from this research by 0.04 Å. The geometric data show very little difference in the angles between Akola and this work, aside from the torsional angle of the Akola study being slightly closer to planarity, implying that the geometries are approximately similar, the geometry in this work being slightly more compact.

3.1.3 Other Constitutional Isomers

It should be noted that the geometry of D_{2d} and D_{4h} structures were optimized but harmonic vibrational frequency computations found an imaginary vibrational mode for each of these structures, and they are not reported as valid local minima. Both isomers preferred to form a bond between two central bismuth atoms and descend along their PES to the C_{2v} isomer.

3.1.4 Bismuth Dimer

The geometry and vibrational frequency of Bi_2 were computed in this research to affirm the validity of the later energetics. The bond length was computed to be 2.679 Å and the fundamental frequency was computed to be 183.7 cm^{-1} utilizing CCSD(T)/cc-pVQZ-PP with the same large core ECP used in the T_d and C_{2v} Bi_4 optimizations. Gerber and Broida report the experimental bond length to be 2.6597 Å[62] and Effantin et al.[63] deduce the Bi_2 harmonic vibrational frequency to be 173 cm^{-1} from experiment.[63] The methods used in this paper provide reasonable agreement with experiment for Bi_2 and so confidence may be placed in the values computed for the T_d and C_{2v} structures.

3.2 Vibrational Frequencies

3.2.1 T_d Structure

While many studies have reported the geometry of the T_d isomer, only three others[14,19,60] have reported its vibrational frequencies. This should come as no surprise because Bi_4 is a system with massive nuclei and so its vibrational potential energy wells will be shallow, making the computation of vibrational frequencies challenging. VPT2 corrections were made to the computed harmonic frequencies in this study in order to obtain fundamental frequencies for the T_d structure. The previous three studies report only harmonic frequencies.

The harmonic vibrational frequencies reported by other studies agree well with those computed in this study. The three vibrational modes are computed to be 168, 95, and 123 cm^{-1} in this work (listed in Table 1) as compared to 165, 94, and 124 cm^{-1} (Jia et al.)[14] and 163, 93, and (120,122) cm^{-1} (Akola).[19] Akola reported a splitting of 2 cm^{-1} in ω_2, which is likely a slight geometric distortion due to numerical imprecision. Liang et al. report only one IR active vibrational frequency at 115 cm^{-1} which likely corresponds to ω_3.[60]

The only IR-active vibrational mode for T_d Bi_4 is v_3. This vibrational feature could be used to confirm the presence of the T_d structure of the Bi_4 molecule. According to two mass spectrometry studies,[5,7] utilizing heat and laser vaporization respectively, Bi_2 and Bi_4 are produced in greatest abundance with very small amounts of Bi_3 and Bi_5. Many studies report vibrational frequencies for Bi_3.[19,24–26,60,64] However, only one fundamental, computed by Choi et al.,[64] is close enough to interfere with the detection of the T_d vibrational band (v_3). This vibrational frequency has a value of approximately 124 cm^{-1}. According to Choi et al. this fundamental is not IR active (infrared intensity of 0). Additionally, Choi et al. report very low infrared intensities for the rest

Table 3 Valence focal point analysis of the relative energy $T_d \longrightarrow C_{2v}$ in kcal mol^{-1}. Delta (δ) denotes the change in relative energy (ΔE_e) with respect to the preceding level of theory

	HF	$+\delta$MP2	$+\delta$CCSD	$+\delta$(T)	$+\delta$T	$+\delta$(Q)	$+\delta$Q	Net
cc-pVDZ-PP	+46.41	−6.92	+1.98	−4.20	−0.44	−1.88	+0.53	[+35.48]
cc-pVTZ-PP	+46.39	−4.43	+0.96	−3.72	−0.32	−1.95	[+0.53]	[+37.46]
cc-pVQZ-PP	+45.58	−3.27	+0.95	−3.51	[−0.32]	[−1.95]	[+0.53]	[+38.01]
cc-pV5Z-PP	+45.43	−2.88	+0.99	−3.44	[−0.32]	[−1.95]	[+0.53]	[+38.37]
CBS	[+45.40]	[−2.47]	[+1.04]	[−3.36]	[−0.32]	[−1.95]	[+0.53]	[+38.87]

$\Delta E_e(\text{final}) = \Delta E_e[\text{CCSDTQ/CBS}] + \Delta_{\text{ZPVE}}[\text{CCSD(T)/cc-pVQZ-PP}] + \Delta_{\text{DBOC}}[\text{HF/cc-pVTZ-PP}] + \Delta_{\text{rel}}[\text{CCSD(T)/cc-pVTZ-PP}]$
$\Delta E_e(\text{final}) = 38.87 - 0.15 + 0.01 + 0.00 = \mathbf{38.73}$ kcal mol^{-1}

Table 4 Valence focal point analysis of the relative energy $Bi_4(T_d) \longrightarrow 2\,Bi_2$ in kcal mol^{-1}. Delta (δ) denotes the change in relative energy (ΔE_e) with respect to the preceding level of theory

	HF	$+\delta$MP2	$+\delta$CCSD	$+\delta$(T)	$+\delta$T	$+\delta$(Q)	$+\delta$Q	Net
cc-pVDZ-PP	+60.56	−11.53	−0.86	−1.60	−0.71	−1.28	+0.19	[+44.76]
cc-pVTZ-PP	+63.01	−1.14	−2.74	−0.43	−0.88	−1.23	[+0.19]	[+56.77]
cc-pVQZ-PP	+62.69	+3.18	−3.13	+0.26	[−0.88]	[−1.23]	[+0.19]	[+61.08]
cc-pV5Z-PP	+62.63	+4.61	−3.05	+0.58	[−0.88]	[−1.23]	[+0.19]	[+62.84]
CBS	[+62.62]	[+6.11]	[−2.98]	[+0.91]	[−0.88]	[−1.23]	[+0.19]	[+64.74]

$\Delta E_e(\text{final}) = \Delta E_e[\text{CCSDTQ/CBS}] + \Delta_{\text{ZPVE}}[\text{CCSD(T)/cc-pVQZ-PP}] + \Delta_{\text{DBOC}}[\text{HF/cc-pVTZ-PP}] + \Delta_{\text{rel}}[\text{CCSD(T)/cc-pVTZ-PP}]$
$\Delta E_e(\text{final}) = 64.74 - 0.51 - 0.21 + 0.00 = \mathbf{64.02}$ kcal mol^{-1}

of the Bi_3 frequencies, the largest intensity being 0.01 km mol^{-1} for modes with frequencies of about 161 and 163 cm^{-1}. In conjuction with the low abundance of Bi_3 and Bi_5, it is unlikely that any other vibrational frequencies will overlap with ν_3 for T_d Bi_4 and its detection will confirm the presence of the T_d structure.

Anharmonic corrections are computed for the T_d isomer and found to slightly lower each harmonic frequency. VPT2 did not explicitly treat this system as a spherical rotor. However the anharmonic correction to the degenerate modes was identical across all three of the t_2 and both of the e degenerate vibrational modes. The corrections display a linear increase in absolute value as the harmonic frequency energies get larger. The harmonic frequencies computed in this work appear to be a good approximation for the frequencies of the T_d isomer as the largest anharmonic correction is -1 cm^{-1}.

3.2.2 C_{2v} structure

The C_{2v} isomer vibrational frequencies have been reported in only one other study.[19] Akola reported vibrational frequencies of 142, 76, 58, 89, 124, and 104 cm^{-1} for modes one through four, while this work predicts them to be 148, 84, 49, 100, 132, and 108 cm^{-1} (listed in Table 2). There is a range of deviation between this study and Akola of 6-11 cm^{-1}, with most of Akola's frequencies being smaller aside from ω_3. This ω_3 vibrational mode corresponds to a 'flapping' motion of the C_{2v} structure. This disparity in the trend could stem from the difference in torsional angle between the two geometries, as the Akola geometry is slightly closer to planarity than the geometry of this work. Another possible contributing factor could be that the geometry of this work is wider set, as the 'wing' atoms are predicted to be 4.5 Å apart with a torsion angle (τ_{4213}) of 57.8°and Akola predict this distance to be 4.6 Å with a τ_{4213} of 57.7°. Our structure is virutally identical to Akola.

3.3 Energetics

In addition to geometries and harmonic frequencies, the energy difference between the two isomers, the dissociation energy of T_d Bi_4 into two Bi_2 molecules, and the dissociation of Bi_2 into two Bi atoms have been computed. Both of these values were obtained by employing the focal point analysis method discussed in the Theoretical Methods section.

From Table 3 it may be seen that after extrapolating out to the CCSDT(Q)/CBS level of theory the energy difference between the T_d and C_{2v} isomers is +38.87 kcal mol^{-1}. This large total energy difference suggests that the T_d isomer would exist in vast excess compared to the C_{2v} isomer. This energy can then be augmented by a DBOC of +0.01 kcal mol^{-1} and a harmonic ZPVE correction of -0.15 kcal mol^{-1} (the relativistic correction is already accounted for in the ECP) yielding a final energy difference of +38.73 kcal mol^{-1}. The absolute DBOCs for the T_d and C_{2v} structures are 0.51 kcal mol^{-1} and 0.52 kcal mol^{-1}, respectively. Stability analysis was performed on the T_d structure and a nearby $^1A_1$ state (contained within a $^3T_1$ state) was identified that may be contributing to a Jahn-Teller distortion, leading to a large DBOC for both structures.

The dissociation energy of Bi_4 into two Bi_2 molecules is shown in Table 4. This dissociation energy is extrapolated out to the same level of theory as the constitutional isomerization energy

Table 5 Valence focal point analysis of the relative energy $Bi_2 \longrightarrow 2\,Bi$ in kcal mol^{-1}. Delta (δ) denotes the change in relative energy (ΔE_e) with respect to the preceding level of theory

	HF	$+\delta$MP2	$+\delta$CCSD	$+\delta$(T)	$+\delta$T	$+\delta$(Q)	$+\delta$Q	Net
cc-pVDZ-PP	−27.85	+65.95	−10.13	+7.27	+0.11	+1.58	−0.26	[+36.67]
cc-pVTZ-PP	−24.85	+72.92	−11.00	+8.57	−0.36	+1.92	[−0.26]	[+46.95]
cc-pVQZ-PP	−23.81	+76.89	−11.94	+9.20	[−0.36]	[+1.92]	[−0.26]	[+51.65]
cc-pV5Z-PP	−23.66	+79.25	−12.75	+9.43	[−0.36]	[+1.92]	[−0.26]	[+53.58]
CBS	[−23.64]	[+81.73]	[−13.59]	[+9.68]	[−0.36]	[+1.92]	[−0.26]	[+55.49]

$\Delta E_e(\text{final}) = \Delta E_e[\text{CCSDTQ/CBS}] + \Delta_{\text{ZPVE}}[\text{CCSD(T)/cc-pVQZ-PP}] + \Delta_{\text{DBOC}}[\text{HF/cc-pVTZ-PP}] + \Delta_{\text{rel}}[\text{CCSD(T)/cc-pVTZ-PP}]$
$\Delta E_e(\text{final}) = 55.49 - 0.26 - 0.15 - 0.01 = \mathbf{55.07}$ kcal mol^{-1}

change and the result is an energy difference of +64.74 kcal mol^{-1}. A large DBOC of −0.21 kcal mol^{-1} (the relativistic correction again being negligible) can be applied alongside an anharmonic ZPVE correction of −0.51 kcal mol^{-1} to yield a corrected dissociation energy of +64.02 kcal mol^{-1}. It should be noted that this computed dissociation energy of Bi_4 into two Bi_2 molecules does not agree with the experimental value of Kohl et al.[2] They report a second-law $Bi_4 \rightarrow 2Bi_2$ dissociation energy of 43.82±1.10 kcal mol^{-1} at 298 K. This deviation of 20 kcal mol^{-1} from Theory is rather large.

In our initial computations, we used the 78 electron bismuth pseudopotential of Dolg and coworkers.[33] However, this method produced a dissociation energy for diatomic Bi_2 of 70 kcal mol^{-1}, as opposed to the experimental value of 48 kcal mol^{-1} reported by Ehret and Gerber[65] at an unspecified temperature as well as an experimental value reported by Kohl et al.[2] of 47 kcal mol^{-1} at 298 K utilizing ion intensities from mass spectrometry. All dissociation energies computed in this paper are at 0 K. Assuming the experimental dissociation energy is correct, such agreement is not acceptable. This led to a careful consideration of the 2010 paper of Peterson and Yousaf.[66] The latter authors used the 60 electron ECP of Dolg and coworkers,[33] with large valence and core-valence basis sets and correlating all electrons outside the 60 electron small core. In this way Peterson and Yousaf predicted the Bi_2 dissociation energy to be 62 kcal mol^{-1} with the CCSD(T)/CBS(45) method. The latter result we consider the basis set limit for CCSD(T) when only scalar relativistic effects are considered. The 2012 paper of Hofener, Ahlrichs, Knecht, and Visscher[67] included relativistic effects at a higher level and predicted a Bi_2 dissociation energy of 50 kcal mol^{-1}, very close to experiment. Neither Bi_2 in its ground state or the Bi atom in its ground ^{4}S state has spin-orbit coupling to first order of perturbation theory. Thus the dissociation energy difference of 12 kcal mol^{-1} between the Peterson-Yousef and Hofener-Ahlrichs-Knecht-Visscher predictions seems large. The deviation between experiment and high-level theory is a little larger at about 15 kcal mol^{-1}, which is puzzling.

The methodology used here incorporated the 60 electron ECP of Dolg and coworkers,[33] but we only correlated the outer five electrons for each bismuth atom. Our extrapolated CCSDTQ/CBS dissociation energy for Bi_2 is 55.07 kcal mol^{-1}, in reasonable agreement with the 62 kcal mol^{-1} in the more complete theoretical treatment of Peterson and Yousaf.[66] Although a more complete treatment of relativistic effects would be good, for the Bi_4 system this seems challenging with our computational resources.

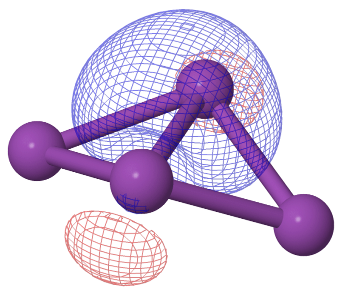
The vertical electronic excitation energies for both isomers were computed and found to be 156 kcal mol^{-1} for the electronic transition from the T_d electron configuration to the C_{2v} electron configuration at the T_d equilibrium geometry computed in the present research. An energy difference of 9 kcal mol^{-1} was found for the electronic transition from the C_{2v} electron configuration to the T_d electron configuration at the C_{2v} equilibrium geometry. Thus there must be a crossing of these potential energy surfaces somewhere between these minima. While this phenomenon is not explored further in the present research, a future study could be done that examines the transition between the two isomers using multireference methods to compute both diabatic and adibatic potential energy surfaces between the isomers.

3.4 NBO analysis

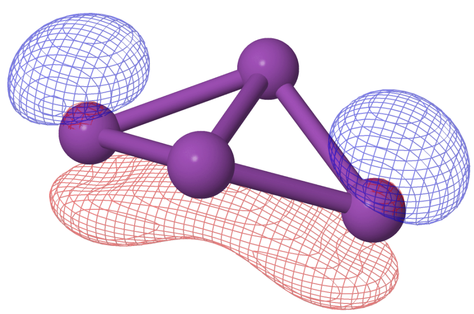
Natural Bond Orbital (NBO) analyses were performed on both the T_d and C_{2v} isomers. The results obtained for the T_d isomer showed that the six bonds were almost doubly occupied (1.98) with four lone pairs being essentially doubly occupied (2.00). This bonding pattern matches exactly the conventional view of a group 5 T_d tetramer, such as P_4.

The C_{2v} structure, however, yields a fascinating result. The two bismuth atoms at the tips of the 'wings' (atoms 3 and 4 in Fig. 2 of the C_{2v} structure) have a "non-Lewis" bond connecting them with an occupancy of 0.51. We attribute this "non-Lewis"[34] interaction to long-bonding, a phenomenon recently explored by Landis and Weinhold.[68] This long-bonding orbital has primarily atomic p-orbital character. Landis and Weinhold stress the necessity of lowering the energy of the long bond through an intermediary electron density donating source. In the C_{2v} isomer of Bi_4, a Lewis bond between the 'spine' atoms, atoms 1 and 2 in Fig. 2, appears to be the primary donator of electron density. This deduction was made due to the aforementioned Lewis bond being geometrically in the correct position to donate electron density to the 'long-bond' and the occupancy of the orbital denoted in Figure 3(a) being 1.61. These 'wing' atoms are 4.580 Å apart, approximately 1.6 Å longer than the T_d bond distance of 3.016 Å. The NBO described by the in-phase p-orbitals on atoms 3 and 4 has an occupancy of 1.77, and it is reasonable to say that this

NBO also donates a small amount of electron density to the long bond. This is due to its geometric and energetic proximity to the long-bond, as well as the other higher energy NBOs not having enough collective occupancy to fully explain the in-phase NBO's occupancy deficiency.



(a) The Lewis NBO of the C_{2v} isomer.



(b) The non-Lewis, long-bonding NBO of the C_{2v} isomer.

Fig. 3 The Lewis NBO in (a) donates electron density into the non-Lewis NBO shown in (b). It is most likely that the electron density is donated by the overlap of the blue lobes of the two NBOs. Note that atoms 3 and 4 at the tips of the 'wings' of the C_{2v} isomer are separated by a distance of 4.488 Å.

This C_{2v} structure 'long-bond' appears to be the energy lowering factor that distinguishes the C_{2v} structure as a local minimum where neither the D_{4h} nor D_{2d} structures are local minima. The extreme distance between the non-bonding bismuth atoms and the lack of an electron density donator for the D_{4h} and D_{2d} structures do not allow them to take advantage of this energy lowering effect. While no computations were performed on the Bi_4 anion in this work, it may be speculated that the C_{2v} isomer which is reported to be the global minimum of the Bi_4 anion by Gausa et al.,[16] is so because more electron density may then be donated into the long-bond, thus lowering the energy of this isomer. This does not explain, however, why the D_{2d} isomer was reported as a global maximum for this anion in the study by Jia et al.,[14] and more work should be done to assert the validity of the C_{2v} structure 'long-bond'. The T_d isomer is likely not the global minimun for the Bi_4 anion because its extra electron density will be donated into the antibonding orbital that pushes the T_d isomer into the C_{2v} isomer by splitting a Bi-Bi bond.

4 Conclusions

Two constitutional isomers of Bi_4 of T_d and C_{2v} symmetry were explored in this study. These two structures were found to be local minima while the D_{4h} and D_{2d} isomers were determined to be first-order saddle points. The optimized geometry of the T_d isomer can be fully described by the Bi-Bi interatomic radius, which is computed to be 3.016 Å and this leads to a more compact structure than reported in prior studies. The harmonic vibrational frequencies of the T_d isomer are computed to be, in general, larger than those of prior studies. The present research is the first to predict fundamental vibrational frequencies of Bi_4 (T_d). The optimized geometry of the C_{2v} isomer computed in this research was found to be more compact than the geometry from a prior study,[19] while the two theoretical geometries have nearly identical conformational structures. The C_{2v} isomer is found to have higher harmonic vibrational frequencies in all modes but one, the ω_3 mode. The T_d and C_{2v} isomer energy difference was computed as +39 kcal mol^{-1}, with the T_d isomer being lower in energy. The dissociation of Bi_4 (T_d) into two Bi_2 molecules was computed to have an energy of +65 kcal mol^{-1}. The dissociation of Bi_2 was computed to have an energy of +55 kcal mol^{-1}, which is a significant deviation from an experimental value of 48 kcal mol^{-1}[65] and a theoretical value including spin-orbit effects of 50 kcal mol^{-1}.[67] This discrepency warrants further research. Through NBO analysis, the C_{2v} isomer of Bi_4 was found to exhibit 'long-bonding' between the furthest apart 'wing' atoms. This 'long-bonding' is facilitated by the σ-bonding orbital between the 'spine' atoms of the C_{2v} isomer.

Finally, we point to the obvious way to spectroscopically observe the bismuth tetramer. The t_2 symmetry ν_3 fundamental predicted at 123 cm^{-1} has a moderate IR intensity, namely 0.23 km mol^{-1}. This Bi_4 fundamental is well separated from the previously observed Bi_2 (173 cm^{-1}) and Bi_3 (161, 163 cm^{-1}) vibrational frequencies.

Conflicts of interest

There are no conflicts to declare.

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