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Infrared and Raman spectra of trimethoxyborane isotopomers and quantum-chemical studies of structure and force field

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ABSTRACT

Infrared and Raman spectra in the gas phase are reported for trimethoxyborane, $B(OCH_3)_3$, and its ${}^{13}C_3$ and d_9 isotopomers. Some liquid phase Raman data were also obtained. Quantum-chemical (QC) studies of structure and force field have been made with B3LYP and MP2 models. These studies highlight the change in configuration of the methyl groups with change in basis set, within the C_{3h} point group. Scaled QC force fields together with the new spectra enable assignments of fundamental bands to be improved. A Fermi resonance involving v_{12} is examined. The difference in strength between the two types of C–H bond in each methyl group is reckoned to be rather less than that deduced earlier from IR spectra of $B(OCHD_2)_3$. This conclusion is supported by QC data for dimethylether.

MP2 estimates of certain interaction force constants are superior to those from B3LYP calculations. Abnormal scale factors for the torsional motion involving the O–B–O–C system identify deficiencies in the QC models employed.

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1. Introduction

The molecule of trimethoxyborane (TMB) has been the subject of a number of structural and spectroscopic studies [1–9]. Planarity of the heavy atom skeleton is expected on chemical grounds and has been verified in gas phase electron diffraction (ED) studies [1,2]. However, the orientation of the methyl groups has been the subject of dispute. In the ED study, these groups were considered to be twisted in such a way that the overall symmetry of the molecule was $C_{3,}$ in contrast to the C_{3h} point group which would be expected if an equivalent CH bond in each group lay in the skeletal plane. Earlier vibrational spectra were interpreted on the basis of such a C_{3h} structure [3]. Non-equivalence of the CH bonds in each methyl group has been demonstrated in two ways, firstly by measuring the infrared spectra of the partially substituted species $B(OCHD_2)_3$ in the gas phase [4] and secondly, by a study of the CH stretching overtones of the parent molecule [5]. The latter study also included a calculation of the equilibrium geometry by a quantum-chemical (QC) HF/3-21G calculation. Both of these studies indicated the presence of two types of C-H bond, a single strong one lying in the skeletal plane (CH^s) and two weak ones positioned symmetrically above and below this plane (CH^a). In the C_{3h} structure from the HF/3-21G calculation, the in-plane C-H^s bond was oriented *cis* relative to the boron atom. This structure contrasted with an earlier theoretical calculation which yielded a C_3 point group [6]. Accompanying a reinvestigation of the Raman and infrared spectra of the parent molecule, a wider Hartree–Fock study was made of the various possible conformations using the basis sets, 3-21G, 4-21G and 6-31G* [7]. With the 3-21G basis, the lowest energy was again obtained with the C_{3h} (C–H^s cis to B) structure. However with the 4-21G and 6-31G* basis sets the *trans* structure became the stable form. This structure is illustrated in Fig. 1.

Ab initio force constants from the HF/3-21G calculation were then used in [7] in conjunction with a crude scaling procedure to interpret the observed spectra and suggest locations of unobserved fundamental frequencies.

The change of structure in the molecule of TMB has also been explored in an unpublished study by Willetts [8]. Using a double zeta basis, Willetts found that insertion of a polarisation function onto each oxygen atom was enough to produce the stability switch from *cis* to *trans*. At the same time there was a marked decrease of \sim 4° to 5° in the BOC angles in both forms. This led to the suggestion that the erroneously large ∠BOC in the *cis* form found when the polarisation function was absent, was enough to relieve a repulsion between the H^s hydrogen atom and the neighbouring oxygen which, when present, rendered the *trans* form more stable. A double zeta MP2 calculation with polarisation functions on the oxygen atoms gave the same result [8].

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Fig. 1. Trans-C_{3h} structure of $B(\text{OCH}_3)_3$ as obtained from the MP2/6-311++G** model.

More recently, DFT calculations with a larger basis set (B3LYP/ 6-311G++(d,p), performed to underpin a study of the crystal structure by X-ray and neutron diffraction techniques, has confirmed that in an isolated molecule the CH^s bond lies *trans* to boron [9]. However, in the crystal, the X-ray diffraction evidence pointed to the presence of orientational disorder among the methyl groups.

The present investigation is both theoretical and experimental. In the theoretical part, HF, B3LYP and MP2 methods were used with a variety of basis sets to provide further evidence for the stability of the *trans*- C_{3h} structure and also to provide harmonic force fields. The latter were then used after careful scaling to observed frequencies to improve the interpretation of the vibrational spectra and the prediction of unobserved fundamental frequencies. This process was aided by accompanying QC calculations of infrared and Raman intensities.

The experimental part involved new spectra of the parent (d_0), $B(O^{13}CH_3)_3(^{13}C)$ and $B(OCD_3)_3$ (d_9) substituted isotopomers. Some of the infrared spectra of d_0 and d_9 involved have previously been reported and some assignments made [4]. However, their detailed interpretation had earlier proved impossible, when only empirical force fields had been available. The addition of Raman spectra, obtained in both gas and liquid phases, and of data for the ^{13}C isotopomer, together with our QC calculations has enabled a deeper though still incomplete understanding of the spectra to be obtained.

2. Experimental

Samples of TMB were prepared by reacting BCl_3 with a slight excess of the appropriately labelled methanol, as described by Wiberg and Sütterlin [10]. Traces of methanol proved hard to remove by fractional condensation, but their residual bands were readily identified. The presence of a further impurity was indicated by the observation of very weak, polarised Raman bands in both phases, seen in the gas at 774 and 451 cm⁻¹ (d₀), 767 and 446 cm⁻¹ (¹³C) and 736 cm⁻¹ (d₉). A likely source of these bands is the compound (HO)B(OMe)₂, for which a Raman band at 773.8 cm⁻¹ has been reported [11].

Infrared spectra were recorded in the 4000–400 cm⁻¹ region on a Nicolet 7199 FTIR spectrometer at a resolution of 0.5 cm⁻¹. Between 650 and 50 cm⁻¹ a Nicolet 20F bench was employed, the resolution then being 0.7 cm^{-1} .

Gas and liquid phase Raman spectra were recorded on a Spex 1401 double monochromator equipped with an argon-ion laser. Spectra were calibrated against emission lines from a neon lamp. Polarisation information was obtained in the usual way by comparing I_{\perp} and I_{\parallel} spectral intensities.

The band frequencies obtained in this work are given in Tables 1 (d_0) and 2 (d_9) respectively. An infrared survey spectrum, 400 to

 $2400\ \text{cm}^{-1},$ of d_9 is available as Figure S1 in the Supplementary Data.

3. Theoretical

Hartree–Fock (HF), MP2 and B3LYP calculations were performed using the Gaussian programs G98 or G03 [12]. The geometry was studied using basis sets varying from 3-21G to 6-311++G** and cc-pVTZ. This last basis set was used only in conjunction with the B3LYP model. Three calculations of the vibrational force field were made, using respectively B3LYP/6-311++G**, B3LYP/cc-pVTZ and MP2/6-311++G** models.

For convenience in the tables below, $6-311G_{**}$, $6-311++G_{**}$ and cc-pVTZ are abbreviated to, tz (triple zeta), tz+ and cct respectively. The prefix m or d then indicates the method used, MP2 or DFT(B3LYP).

Convergence in the prior geometry optimizations was controlled by the "tight" option. For the density functional calculations a grid of 99 shells, each containing 302 points, was employed.

Repetition of a given calculation from differing starting geometries gave frequencies agreeing within 0.05 cm⁻¹. Bond lengths were similarly reproduced to within about 0.00002 Å. This reproducibility is relevant to our interest in the small differences in properties exhibited by the two types of C–H bond.

Calculations were performed either on a DEC Alpha 1000 work station or using the resources of the EPSRC National Service for Computational Chemistry Software, on Columbus, a cluster of six HP ES40 computers, each of which has four 833 MHz EV68 CPUs and 8 Gbytes of memory.

For the calculation of force constants on a symmetry coordinate basis and subsequent scaling, the Gaussian output of Cartesianbased force constants was input into the program ASYM40 [13]. In order to avoid the use of complex symmetry coordinates in the doubly degenerate E' and E" classes, the procedure devised by Cyvin et al. was followed which uses only real coordinates [3,14]. Our symmetry coordinates were identical in form (though not in numbering) to those listed by Stampf et al. [7] with two exceptions. Our A' and E' CH stretching coordinates were composed of motions of one type of bond only, either CH^s or CH^a, while the τ CH₃ and τ OBOC torsions were defined with a larger number of dihedral angles. Our set of symmetry coordinates, in the form input into ASYM40, is included in Table S1 of the Supplementary Data.

4. Results: QC predictions of structure and vibrational properties

Table 3 shows the relative energies and BOC angles of the *cis* and *trans-C*_{3h} structures found from the HF, B3LYP and MP2 models with various basis sets. All three methods yield a stable *cis* structure only with the 3-21G basis set. For all the larger sets the *trans* structure has the lower energy. Sample calculations found imaginary frequencies for the less stable form, which means that there was no evidence for an additional minimum on the potential surface. However, a more comprehensive study would be needed to establish firmly the absence of such minima. Trial calculations with a C₃ structure and methyl twist angle of 31.6°, as found from the ED study [2], failed to converge and this conformation was not investigated further.

The marked influence of the inclusion of polarisation functions into the basis set, noted by Willetts [8], is clearly visible. However, there is little sign of any consistent change in BOC angle with model or basis which might affect the repulsion between an in-plane H^s atom and the neighbouring non-bonded oxygen. It seems more likely that the stable comformation is dictated by changes in the π electron system.

Table 1

Infrared and Raman frequencies (cm⁻¹) and ¹³C frequency shifts observed in B(O¹²CH₃)₃ and B(O¹³CH₃)₃.

rt*Co	IR(gas)		R(gas)		R(liq)	Assignment ^a
<table-container>1280%100100101<th< td=""><td>v(¹²C)</td><td>$-\Delta v(^{13}C)^{b}$</td><td>v(¹²C)</td><td>$-\Delta v(^{13}C)^b$</td><td>v(¹²C)</td><td></td></th<></table-container>	v(¹² C)	$-\Delta v(^{13}C)^{b}$	v(¹² C)	$-\Delta v(^{13}C)^b$	v(¹² C)	
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$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			1453 m, sp, p	5(1)	1400	$v_{3}(a)$ $v_{4}(a')$
	1393 sh	6(1)			1070 1	$v_{19} (e')^{10} B$
132 w, sh, bd 1330 w, sh, bd 1340 $21_{12}^{15} (\Lambda') \mathbb{R}$? $v_{21} + v_{28}$ (Λ', \mathbb{E}')? 1249 sh 13(1) $v_{7} + v_{22}$ ($\mathbb{E}')$ $v_{7} + v_{22}$ ($\mathbb{E}')$ 1167 sh 1173 w, bd, dp 5(7) v_{11} (x')? 1167 sh 1173 w, bd, dp 5(7) v_{11} (x')? 1112 vw, sh 1121.4 w, p 20(3) 1098 v_6 (x') 1112 vw, sh 1074 vw, p 5(4) McOH McOH 1042 s 18.0(7) 1047 w, bd dp 23(6) $v_{21} + v_{28}$ (v', \mathbb{E}')? 1042 s 18.0(7) 1047 w, p 5(4) McOH 1036 m, p 21(2) 997 vw, p Impurity? 935, 924 w 4.7(7) McOH $v_{21} + v_{28}$ (v', \mathbb{E}')? 869 vw 18(1) 774 vw, p 7(3) 769 Impurity? 780 vvw 9(1) 774 vw, p 7(3) 769 Impurity? 711.4 w, q 3(1) 52, v_2, p 731 vs, p 73(8) 722 v_{12} (x', \mathbb{E}') ¹¹ B R 667.4 m, q 3(1) 524 vw, bd, dp 520 v_{22} (x', \mathbb{E}') ¹¹ B R <td>1384 sh 1363 vs</td> <td>5(7) 6(1)</td> <td></td> <td></td> <td>1378 sn</td> <td>$v_{12} + v_{22} + v_{23}$ (A') FR v_{10} (e') ¹¹B</td>	1384 sh 1363 vs	5(7) 6(1)			1378 sn	$v_{12} + v_{22} + v_{23}$ (A') FR v_{10} (e') ¹¹ B
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			1339 w, sh, bd		1340	$2v_{12} (A') FR ? v_{21} + v_{28} (A'', E'') ?$
1401 in 10(2) 173 w, bd, dp 1132 w, p 5(7) y_{11} (a^{27})? 1167 sh 1132 w, p impurity? impurity? 1112 w, sh 1121.4 w, p 20(3) 1098 y_{6} (a^{7}) 1112 w, sh 1121.4 w, p 20(3) 1098 y_{6} (a^{7}) 1112 w, sh 1074 w, p 5(4) McOH 1042 s 18.0(7) 1047 w, bd dp 23(6) wold 935, 924 w 4.7(7) McOH y_{21} (e^{r}) 869 w 18(1) $y_{21} + y_{22}$ (A^r, E^r) ⁵ $y_{21} + y_{23}$ (A^r, E^r) ⁵ 859 w 9(1) $y_{21} + y_{21}$ (A^r, E^r) ⁵ $y_{21} + y_{23}$ (A^r, E^r) ⁷ 780 vvw 18(1) $y_{21} + y_{21}$ (A^r, E^r) $y_{21} + y_{21}$ (A^r, E^r) 780 vvw 774 vw, p 7(3) 769 B(0)(OthOH)_2 711 w, p 9(5) 693 $y_{22} + y_{21}$ (A^r, E^r) $y_{22} + y_{22}$ (A^r, E^r) 67.4 m, q 3(1) $y_{22} + y_{22}$ (A^r, E^r) $y_{22} + y_{22}$ (A^r, E^r) $y_{22} + y_{22}$ (A^r, E^r) 524.7 m 5(1) 524 w, bd, dp 520 $y_{22} + y_{22}$ (A^r	1249 sh	13(1)				$v_7 + v_{22} (E')$
1132 vw, p 1132 vw, p 1132 vw, p 1132 vw, p 100 1098 Impurity? 1112 vw, sh 1121.4 w, p 20(3) 1098 vs (a') vs (a') 1142 s 1074 vw, p 5(4) McOH 1042 s 180(7) 1036 m, p 23(6) McOH 935, 924 w 4.7(7) McOH McOH 869 vw 18(1) 1042 s 997 vw, p Impurity? 870 vw 9(1) 74 vw, p 7(3) 769 B(OH(OCH3)2 780 vvw 9(1) 753 vvw, p 1mpurity? 1mpurity? 753 vvw, p 731 vs, p 73(8) 722 vz (a') 711 w, p 9(5) 693 224 vs (A', E') ¹⁰ B FR 692 8 w, q 5(1) 524 vw, bd, dp 250 222 (c') 711 w, p 311 vs, p 7(4) 350 222 vs (A', E') ¹¹⁰ B FR 923 M, q 5(1) 524 vw, bd, dp 252 22 (c') 318 vw 1(1) 311 vs, p 6(1) 321 vg (a') 318 vw 1(3) 235 vw, p 1mpurity? 1mpurity? 100 w, bd 0(3) 184 s, bd, dp 3(3) 3(3) Vs (a')	1167 sh	10(2)	1173 w, bd, dp	5(7)		$v_{20}(e)$ $v_{11}(a'')?$
$ \begin{array}{ c c c c c c } 1112 \ w, sh & & & & & & & & & & & & & & & & & & $			1132vw, p			Impurity?
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1112 vw sh		1121.4 w, p	20(3)	1098	$v_6(a')$ $v_{21} + v_{22}(A'' F'')$?
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1112 111, 511		1074 vw, p	5(4)		MeOH
$\begin{array}{ c c c c c c } 1056 \mbox{ in } p & 21(2) & med n \\ 1056 \mbox{ in } p & 21(2) & pert & pert \\ 1056 \mbox{ in } p & 21(2) & pert & pert \\ 1056 \mbox{ in } p & 21(2) & pert & pert \\ 1056 \mbox{ in } p & 21(2) & pert & pert \\ 18(1) & pert & pert & pert \\ 18(1) & pert & pert & pert & pert \\ 18(1) & pert & pert & pert & pert \\ 18(1) & pert & pert & pert & pert \\ 18(1) & pert & pert & pert & pert \\ 18(1) & pert & pert & pert & pert \\ 18(1) & pert & pert & pert & pert \\ 18(1) & pert & pert & pert & pert \\ 18(1) & pert & pert & pert & pert \\ 18(1) & pert & pert & pert & pert \\ 18(1) & pert & pert & pert & pert \\ 18(1) & pert & pert & pert & pert \\ 18(1) & pert & pert & pert & pert & pert \\ 18(1) & pert & pert & pert & pert & pert \\ 18(1) & pert & pert & pert & pert & pert \\ 18(1) & pert & pert & pert & pert & pert \\ 18(1) & pert & pert & pert & pert & pert & pert \\ 19(1) & pert & pert & pert & pert & pert & pert \\ 19(1) & pert & pert & pert & pert & pert & pert \\ 19(1) & pert &$	1042 s	18.0(7)	1047 w, bd dp	23(6)		$v_{21}(e')$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			1050 III, p	21(2)	997 vw, p	Impurity?
869 vw 18(1) $v_{21} - v_{27} (A'', E'')^c$ 835 vw 9(1) $v_8 + v_{22} (E'), v_7 + v_{13} (A'')$ 780 vvw 774 vw, p 7(3) 769 B(OH)(OCH_3)_2 773 vs, p 731 vs, p 7.3(8) 722 $v_7 (a')$ 711.4 w, q 3(1) 693 $v_{22} + v_{23} (A', E')$ $v_{22} + v_{23} (A', E')$ 711.4 w, q 3(1) 524 vw, bd, dp 523 693 $v_{22} + v_{23} (A', E')$ 699.8 w, q 5(1) 524 vw, bd, dp 520 $v_{22} + v_{27} (A'', E'')^{10}$ 667.4 m, q 0.8(6) $v_{12} (a'')^{11}$ B FR $v_{22} (e')$ $v_{22} (e')$ 318 vw 1(1) 311 vs, p 7(4) 350 $2v_{27} (A', E')$ 273 vw 1(3) $21 v_{25} vw, p$ (61) 321 $v_8 (a')$ 273 vw 1(3) $235 vw, p$ $3(3)$ $v_{23} (e')$ $v_{23} (e')$ 190 w, bd 0(3) 184 s, bd, dp $3(3)$ $v_{23} (e')$ $v_{23} (e')$	935, 924 w	4.7(7)				$v_7 + v_{23} (E')$
780 vvw 774 vw, p 7(3) 769 B(OH)(OCH ₃) ₂ 753 vvw, p 731 vs, p 7(3) 769 B(OH)(OCH ₃) ₂ 780 vvw 731 vs, p 7(3) 769 B(OH)(OCH ₃) ₂ 780 vvw 731 vs, p 7(3) 769 B(OH)(OCH ₃) ₂ 780 vvw 731 vs, p 7(3) 769 B(OH)(OCH ₃) ₂ 780 vvw 711 w, p 9(5) 693 v ₂₂ + v ₂₃ (A', E') 711 w, p 9(5) 693 v ₂₂ + v ₂₃ (A', E') 699.8 w, q 5(1) 524 vw, bd, dp v ₁₂ (a'), ¹¹ B FR 524.7 m 5(1) 524 vw, bd, pp 2v ₂₃ (A', E') 524.7 m 5(1) 524 vw, bd, pp 2v ₂₃ (A', E') 318 vw 1(1) 11 vs, p 6(1) 321 v ₈ (a') 273 vw 1(3) 235 vvw, p 264 vvw,p Impurity? 190 w, bd 0(3) 184 s, bd, dp 3(3) v ₂₃ (e')	869 vw 835 vw	18(1) 9(1)				$v_{21} - v_{27} (A'', E'')^{c}$ $v_{8} + v_{22} (E') v_{7} + v_{12} (A'')$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	780 vvw	5(1)				$v_7 + v_{14} (A'')$
755 vw, p 738 v, p 738 v, p 738 v, p 738 v, p 731 vs, p 731 vs, p 738 v, p 722 v ₇ (a') 711.4 w, q 3(1) 693 v ₂₂ + v ₂₃ (A', E') 699.8 w, q 5(1) v ₂₂ + v ₂₇ (A'', E'') ¹⁰ B FR 699.8 w, q 5(1) v ₁₂ (a'), ¹¹ B FR 667.4 m, q 0.8(6) v ₁₂ (a'), ¹¹ B FR 524.7 m 5(1) 524 vw, bd, dp 520 379 vvw, bd, p 2v ₂₂ (A', E') v ₁₂ (a'), ¹¹ B FR 318 vw 1(1) Impurity? 318 vw 1(1) Impurity? 273 vw 1(3) 511 vs, p 273 vw 1(3) 235 vvw, p 190 w, bd 0(3) 184 s, bd, dp 3(3) V V ₂₃ (e')			774 vw, p	7(3)	769	B(OH)(OCH ₃) ₂
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			731 vs, p	7.3(8)	722	$v_7(a')$
711.4 w, q 3(1) $v_{22} + v_{27} (A'', E'')^{-10} B FR$ 699.8 w, q 5(1) $v_{22} + v_{27} (A'', E'')^{-11} B FR$ 667.4 m, q 0.8(6) $v_{12} (a'')^{.11} B FR$ 524.7 m 5(1) 524 vw, bd, dp $v_{12} (a'')^{.11} B FR$ 379 vvw, bd, p $v_{22} (e')$ $2v_{23} (A', E')$ 311 vv, sh, p 7(4) 350 $2v_{27} (A', E')$ 318 vw 1(1) Impurity? Impurity? 273 vw 1(3) 21 vs, p 6(1) 321 vs, g(a') 273 vw 1(3) 235 vvw, p Impurity? Impurity? 190 w, bd 0(3) 184 s, bd, dp 3(3) $v_{23} (e')$			711 w, p	9(5)	693	$v_{22} + v_{23} (A', E')$
667.4 m, q 0.8(6) 524 vw, bd, dp 520 v_{12} (a^{*}), ¹¹ B FR 524.7 m 5(1) 524 vw, bd, dp 520 v_{22} (a^{*}), ¹¹ B FR 331 vw, sh, p 7(4) 350 $2v_{23}$ (A, E') 318 vw 1(1) Impurity? 273 vw 1(3) 235 vvw, p 273 vw 1(3) 235 vvw, p 190 w, bd 0(3) 184 s, bd, dp 3(3) v_{23} (a^{*})	711.4 w, q	3(1) 5(1)				$v_{22} + v_{27} (A'', E'')$ ¹⁰ B FR $v_{22} + v_{27} (A'', E'')$ ¹¹ B FR
524.7 m 5(1) 524 vw, bd, dp 379 vvw, bd, p 520 v_{22} (e') 2 v_{23} (A, E') 318 vw 311 vw, sh, p 7(4) 350 $2v_{27}$ (A', E') 318 vw 1(1) Impurity? Impurity? 273 vw 1(1) 264 vvw, p Impurity? 273 vw 1(3) 235 vvw, p Impurity? 190 w, bd 0(3) 184 s, bd, dp 3(3) v_{23} (e') 102.8 m, sp 1.6(2) 1.6(2) v_{13} v_{23} (e')	667.4 m, q	0.8(6)				$v_{12} (a'')$, ¹¹ B FR
319 vw, bd, p 2v ₂₃ (Å, E') 311 vw, sh, p 7(4) 350 2v ₂₇ (Å, E') 318 vw 1(1) Impurity? Impurity? 311 vs, p 6(1) 321 v ₈ (a') 264 vvw,p Impurity? Impurity? 273 vw 1(3) 235 vvw, p Impurity? 190 w, bd 0(3) 184 s, bd, dp 3(3) v ₂₃ (e') 102.8 m, sp 1.6(2) v ₁₃ (a') v ₁₃ (a')	524.7 m	5(1)	524 vw, bd, dp		520	$v_{22}(e')$
318 vw 1(1) Introduction Introduction 311 vs, p 6(1) 321 v_8 (a') 273 vw 1(3) 264 vvw,p Impurity? 273 vw 1(3) $v_{13} + v_{27}$ (E') 190 w, bd 0(3) 184 s, bd, dp 3(3) 102.8 m. sp 1.6(2) v_{13}			331 vw, sh. p	7(4)	350	$2v_{23}(A', E')$ $2v_{27}(A', E')$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	318 vw	1(1)	,, r			Impurity?
273 vw 1(3) v13 vr v13 vr 235 vvw, p 235 vvw, p Imputity? 190 w, bd 0(3) 184 s, bd, dp 3(3) v23 (e') 102.8 m. sp 1.6(2) v13 vr v13 vr			311 vs, p	6(1)	321 264 yaw p	v ₈ (a') Impurity2
235 vvw, p Impurity? 190 w, bd 0(3) 184 s, bd, dp 3(3) v_{23} (e') 102.8 m. sp 1.6(2) v_{13} (a'')	273 vw	1(3)			20 4 www,p	$v_{13} + v_{27} (E')$
190 w, bd $0(3)$ 184 s, bd, dp $3(3)$ $v_{23}(e')$ 102.8 m. sp 1.6(2) $v_{12}(a'')$	100 11	2(2)	235 vvw, p	2(2)		Impurity?
	190 w, bd 102.8 m, sp	0(3) 1.6(2)	184 s, bd, dp	3(3)		v_{23} (e') v_{12} (a'')

^a Bands not appearing in earlier spectra [3] are labeled "impurity?" or identified as "B(OH)(OCH₃)₂" or "MeOH". ^b In parentheses, the combined uncertainties from the two data subtracted. ^c This assignment yields $v_{27} = 173 \text{ cm}^{-1}$.

Table 2
Infrared and Raman frequencies (cm ⁻¹) observed in B(OCD ₃) ₃

IR		Raman		Assignment
Ga	IS	Gas	Liquid	
22	82 sh			$v_{as}CD_3 + \tau CD_3$
22	45 ms, br	2245 w, dp		v_1 (a'), v_{15} (e'), v_{24} (e''')
22	35.3 ms, q			$v_{9}(a'')$
22	23 sh			
		2183 vw, dp		$2 \times \delta_{as} CD_3$
21	45 m	2146 w, p		$2 \times \delta_{as} CD_3$
20	85 ms	2087 vs, p		$v_2(a'), v_{16}(e')$
19	94 vw			?
19	38 vvw			?
18	94 vvw			?
18	05 vw			
16	70 w			?
16	13 vw			?
15	78 v			?
14	90 sh			?
14	49 vs			$v_{17} (e')^{10} B$
14	03 vs			$v_{17} (e')^{11} B$
13	33 w			
12	83 w			?'
		1176.3 w. p	1165 w. p	$v_{3}(a')$
11	75 sh	, p	, p	?'
11	22 s	1120 w. br. dp	1114 w. dp	$v_{18}(e')$
			1087 sh. p?	$v_{4}(a')$
10	66 w	1067 w. br. dp	1067 m. dp	$v_{5}(a'), v_{10}(a''), v_{10}(e'), v_{25}(e'')$
10	30 vw a		,p	$v_{c} + v_{14} (A'')$
10	01 m	1000 m dp	996 vs. dn	$v_{20}(e')$
98	5 vvw	1000 III, up	000 10, up	CD ₂ OH
00		943 w. sh. p		?
		935 w. p	932 m. p	$v_{e}(a')$
91	9 w br	··, p	, p	$v_{21}(e')$
01	0 11, 51		908 m dn	$v_{21}(e^{-1})$
90	187 sh a		boo iii, up	$v_{26}(c')$ $v_{11}(a'')$
	, 1	901 w p		$v_{e}(a')$
86	1 vvw	, p		CD ₂ OH
85	1 vvw			CD ₂ OH
		736 vw. p	729 vw. p	$B(OH)(OCD_2)_2$?
70	2.0 m. a	, p	· · · · , p	$v_{12} (a'')^{10} B FR$
	,	6847 vs. p	685 vs. p	$v_{7}(a')$
67	'80m a	00 III 10, P	000 10, p	$v_{12} (a'')^{11} FR$
64	8 w br			v_{12} ($a'' = F''$) FR
49	4 w	492 w. dp	495 w. dp	$v_{22} (e')$
		283 s n	289 m n	$v_{a}(a')$
24	5 w	, P	P	$v_{14} + v_{26} (e')$
16	8 m	164 m. bd. dp	177 m. bd. dn	$v_{22}(e'), v_{26}(e'')$
		156 sh	, su, up	?
92	7 m a			V14 (a")
52				14 (~)

Table 4 compares parameters of five of the *trans*-QC structures with the larger bases with those from the ED experiment [1,2]. Agreement on the B–O and C–O lengths is generally good. There is close agreement between the two models on the difference in the two C–H bond lengths, the in-plane C–H^s bond being 0.002–0.003 Å shorter than the out-of-plane C–H^a bond. A similar but slightly smaller difference is computed for the corresponding *cis*- C_{3h} structures, see Table 4. B3LYP values of the BOC angle are con-

Table 4

Comparison of Observed and QC-calculated geometries for the $trans-C_{3h}$ structure of trimethoxyborane.

Parameter ^a	QC mode		obsd ^b			
	dtz	dtz+	dcct	mtz	mtz+	
rB-O	1.3661	1.3671	1.3670	1.3682	1.3699	1.368(2)
rC-0	1.4252	1.4268	1.4232	1.4246	1.4272	1.424(2)
rC-H ^{aa}	1.0936	1.0931	1.0910	1.0932	1.0930	1.106(3)
rC–H ^s	1.0906	1.0904	1.0883	1.0906	1.0907	1.106
⊿rC–H ^{a-s}	0.0029	0.0027	0.0027	0.0026	0.0023	1.106
⊿rC-H ^{a-s} (cis)	0.0020	0.0018	-	0.0020	-	
∠BOC	120.5	120.9	121.0	117 8	118.3	121.0(2)
∠OCH ^s	107.4	107.2	107.4	107.1	106.6	109.0(5)
$\angle OCH^a_a$	111.2	111.1	111.2	111.1	110.9	109.0
$\angle H^{a}CH^{s}$	109.3	109.4	109.3	109.5	109.6	109.9(5)
$\angle H^{a}CH^{a}$	108.4	108.6	108.5	108.5	108.8	109.9
∠BOCH ^s	180.0	180.0	180.0	180.0	180.0	31.6

^a Bond lengths in Å, angles in °. The H^s atom in each methyl group lies in the skeletal plane in each C_{3h} QC structure, but is out of this plane in the C₃ electron diffraction structure. $\Delta rC-H^{a-s}$ from the *cis* structure is included for three models. ^b C₃ structure from [2], assuming C_{3v} local symmetry for the methyl group.

sistently 2–3° larger than the MP2 ones and closer to that observed, which, however carries an uncertainty of two degrees.

The QC-calculated vibrational frequencies and their associated infrared and Raman intensities are listed in Table 5 for the ${}^{11}B(O^{12}CH_3)_3$ and ${}^{11}B(O^{12}CD_3)_3$ isotopomers. Modes are numbered in order of descending frequency.

In order to evaluate the earlier experimental work on the IR spectrum of $B(OCHD_2)_3$ (d₆) [4], we used the mtz+ model to calculate all the harmonic C–H stretching frequencies and some of the associated IR intensities for all the conformers possible with this species. The results are shown in Table 6. We observe firstly an almost complete independence of each vCH frequency on the disposition of the hydrogen atoms in neighbouring methyl groups. This demonstrates that the coupling between vCH motions in different methyl groups is essentially zero. This lack of coupling is also reflected in the virtual degeneracies visible in the A', A'', E' and E''vCH₃ frequencies in Table 5. The vCH and vCD frequencies can be therefore regarded as effectively those of a single methyl group. (A similar virtual degeneracy is found with the out-of-plane methyl rocking modes in the A'' and E'' classes, near 1178 cm⁻¹ in d₀, and 919 cm⁻¹ in d₉.)

The second feature worthy of comment in Table 6 are the computed infrared intensities associated with the unique v^{is} CH transition in a conformer which has only one C–H^s or C–H^a bond present. These show only a modest variation with orientation. However, the third and critical feature of Table 6 is the change in frequency with orientation. This averages to 29.0 cm⁻¹ from the mtz+ treatment (corresponding dtz+ value 32.5 cm⁻¹). This is substantially less than the previous experimental value of about 62 cm⁻¹ for v^{is} CH^s – v^{is} CH^a [4].

This discrepancy prompted us to test the validity of these QC predictions for the CH bonds in TMB by making similar QC calcula-

Table 3

Relative energies and BOC angles for the *cis*- and *trans*-C_{3h} structures of trimethoxyborane, from HF, B3LYP and MP2 models.

Basis	$\Delta E(cis-tran)$	$\Delta E(cis-trans)$ (kJ mol ⁻¹)		∠BOC (°)					
	HF	B3LYP	MP2	trans HF	cis HF	trans B3LYP	cis B3LYP	trans MP2	<i>cis</i> MP2
3-21G	-1.80	-5.17	-4.19	122.9	124.2	120.0	121.2	119.0	120.4
6-31G	1.11	-	-	125.1	126.4	-	-	-	-
6-31G*	5.92	1.24	3.98	121.6	124.0	120.4	122.4	118.2	120.8
6-311G**	5.30	0.97	4.54	121.8	124.1	120.5	122.4	117.8	120.4
6-311++G**	6.07	2.45	5.28	-	-	120.9	122.7	117.8	120.9
cc-pVTZ	-	2.49	-	-	-	121.0	123.0	-	-

Table 5

Comparison of frequency data from QC calculations, experiment and refinement fit for the d_0 and d_9 isotopomers.

	Mode	ω_{mtz+}^{a}	ω_{dtz+}^{a}	ω_{dcct}^{a}	R _{dt}	z+ ^b	vobsd ^c	v, ϵ_{mtz+}^{d}	v, ϵ_{dtz+}^{d}	v, ϵ_{dcct}^{d}	Motion
Α'											
do	V1	3189	3114	3109	95		_	3001.8	3005.2	3005.3	vCH ^s
u 0	V2	3080	3026	3025	475	5	-	2899.1	2919.9	2923.6	v _e CH ^a
	V3	1528	1502	1506	2		1471	-7.5	-5.0	-4.1	δ _{as} CH ₃
	Va	1505	1481	1485	1		1453	-1.9	-0.7	-0.4	δ _s CH ₃
	V5	1252	1235	1241	0.4		1208	1217.1	1225.3	1227.5	$\rho CH_3, \nu CO$
	v ₆	1149	1129	1135	4		1121.4	-1.9	-0.9	-0.9	vCO, ρ CH ₃
	v7	752	734	737	10		731.4	-0.8	-0.4	-0.2	vBO, vCO
	v ₈	311	297	298	2		311.0	-0.8	-0.8	-0.9	δBOC
do	V.	2368	2311	2308	43		_	2253 5	2255 5	2255 3	vCD ^s
ug	V2	2207	2168	2167	24	1	_	2100.2	2114.6	2117 3	v CD ^a
	V_2	1203	1184	1189	21	•	11763	17	0.1	0.5	$v_{s}CD_{2}$
	V.4	1119	1101	1110	02		1087	36	-12	-17	$\delta_{2}CD_{2}$ vBO
	v=	1099	1081	1085	2		1067	3.3	4.9	4.4	δ ₂ -CD ₂
	V6	960	941	994	4		935	1.0	0.4	0.5	ρCD ₃ , νCO
	v7	704	688	690	8		684.7	0.2	0.7	0.4	vBO, vCO, ρ CD ₃
	v ₈	281	270	270	2		283	0.7	0.8	0.8	δΒΟϹ
							c	d	đ	d	
Species	Mode	ω_{mtz+}^{a}	ω_{dtz+}^{d}	ω_{dcct}	A_{d}	ltz+	Vobsd	v, ϵ_{mtz+}	v, ϵ_{dtz+}^{u}	v, ϵ_{dcct}^{u}	Motion
Α"											
do	v9	3167	3088	3083	10)2	2980.2	0.0	0.0	0.0	$v_{as}CH_2^a$
	v ₁₀	1515	1495	1499	20)	-	1477.2	1477.4	1476.8	$\delta_{as}CH_3$
	v ₁₁	1199	1178	1184	2		-	1176.2	1174.5	1174.3	$\rho'' CH_3$
	v ₁₂	682	681	676	57	7	673 ^t	-0.1	-0.3	-0.4	δBO_3
	v ₁₃	100	106	105	14	1	102.8	-2.0	-0.4	-0.4	τ OBOC, τ CH ₃
	V14	42	51	61	0		49	0.6	0.0	0.0	τCH_3 , $\tau OBOC$
d9	v ₉	2350	2292	2288	62	2	2235.3	2236.8	2236.5	2236.4	$v_{as}CD_2^a$
	v ₁₀	1094	1079	1083	8		1066	0.0	0.0	0.0	$\delta_{as}CD_3$
	V11	926	911	915	8		908.7	-0.1	0.0	0.0	$\rho'' CD_3$
	v ₁₂	680	678	673	53	3	671 ^f	0.3	0.3	0.3	δBO_3
	v ₁₃	88	95	94	11		92.7	1.9	0.5	0.5	τ OBOC, τ CD ₃
	v ₁₄	30	36	43	0		-	35.3	34.7	34.7	τCD_3 , $\tau OBOC$
Species	Mode	(i) a	m, a	m. ^a	A. e	R. b	v.,.c	ve d	ve. d	ve. d	Motion
Species	woue	tomtz+	Wdtz+	Wdcct	ndtz+	Adtz+	Vobsd	v,c _{mtz+}	v,cdtz+	v, edcct	WOUGH
E'		0100									
d ₀	v ₁₅	3189	3114	3109	96	148		3001.7	3005.0	3005.3	vCH^{s} , $v_{s}CH_{2}^{a}$
	v ₁₆	3080	3025	3024	175	0.1		2000 4	20100		
	V			5021	175	0.1		2898.4	2918.9	2922.5	$v_{\rm s} C n_2$, $v C n$
	·1/	1534	1512	1519	264	2	1494	2898.4 0.8	2918.9 0.7	2922.5 -1.0	δ_{s} CH ₂ , VCH δ_{s} CH ₃ . VBO
	v ₁₈	1534 1524	1512 1498	1519 1502	264 14	2 21	1494 1485	2898.4 0.8 4.0	2918.9 0.7 2.6	2922.5 -1.0 3.2	$\delta_{s}CH_{3}$, νBO $\delta_{as}CH_{3}$, $\delta_{s}CH_{3}$
	v ₁₈ v ₁₉	1534 1524 1393	1512 1498 1369	1519 1502 1378	264 14 1167	2 21 2	1494 1485 1363	2898.4 0.8 4.0 0.4	2918.9 0.7 2.6 9.9	2922.5 -1.0 3.2 11.0	$v_s CH_2$, vCH $\delta_s CH_3$. vBO $\delta_{as} CH_3$, $\delta_s CH_3$ vBO, $\delta_s CH_3$
	V ₁₈ V ₁₉ V ₂₀	1534 1524 1393 1213	1512 1498 1369 1194	1519 1502 1378 1200	264 14 1167 30	2 21 2 9	1494 1485 1363 1200	2898.4 0.8 4.0 0.4 7.5 2.8	2918.9 0.7 2.6 9.9 8.8	2922.5 -1.0 3.2 11.0 8.1	v_{s} CH ₂ , vCH δ_{s} CH ₃ . vBO δ_{as} CH ₃ , δ_{s} CH ₃ vBO, δ_{s} CH ₃ ρ CH ₃ ν CO
	V ₁₇ V ₁₈ V ₁₉ V ₂₀ V ₂₁	1534 1524 1393 1213 1071 530	1512 1498 1369 1194 042	1519 1502 1378 1200 1047	264 14 1167 30 156	2 21 2 9 6	1494 1485 1363 1200 1042.4 534.7	2898.4 0.8 4.0 0.4 7.5 2.8	2918.9 0.7 2.6 9.9 8.8 9.0	2922.5 -1.0 3.2 11.0 8.1 8.7 21.2	v_s CH ₂ , vCH δ_s CH ₃ , vBO δ_{as} CH ₃ , δ_s CH ₃ vBO, δ_s CH ₃ ρ CH ₃ vCO δ_s OPO SPOC
	V17 V18 V19 V20 V21 V22 V22	1534 1524 1393 1213 1071 530 197	1512 1498 1369 1194 042 522 173	1519 1502 1378 1200 1047 523 173	264 14 1167 30 156 25	2 21 2 9 6 2 08	1494 1485 1363 1200 1042.4 524.7 190	2898.4 0.8 4.0 0.4 7.5 2.8 -5.6 1.8	2918.9 0.7 2.6 9.9 8.8 9.0 -21.7 6.0	2922.5 -1.0 3.2 11.0 8.1 8.7 -21.3 5.8	δ_{s} CH ₂ , vCH δ_{s} CH ₃ , vBO δ_{as} CH ₃ , δ_{s} CH ₃ vBO, δ_{s} CH ₃ ρ CH ₃ vCO δ OBO, δ BOC δ BOC δ OBO
	v ₁₇ v ₁₈ v ₁₉ v ₂₀ v ₂₁ v ₂₂ v ₂₃	1534 1524 1393 1213 1071 530 197	1512 1498 1369 1194 042 522 173	1519 1502 1378 1200 1047 523 173	264 14 1167 30 156 25 9	2 21 2 9 6 2 0.8	1494 1485 1363 1200 1042.4 524.7 190	2898.4 0.8 4.0 0.4 7.5 2.8 -5.6 1.8	2918.9 0.7 2.6 9.9 8.8 9.0 -21.7 6.0	2922.5 -1.0 3.2 11.0 8.1 8.7 -21.3 5.8	δ_{s} CH ₂ , vCH δ_{s} CH ₃ , vBO δ_{as} CH ₃ , δ_{s} CH ₃ vBO, δ_{s} CH ₃ vCO δ OBO, δ BOC δ BOC, δ OBO
d ₉	V17 V18 V19 V20 V21 V22 V23 V15	1534 1524 1393 1213 1071 530 197 2368	1512 1498 1369 1194 042 522 173 2311	1519 1502 1378 1200 1047 523 173 2307	264 14 1167 30 156 25 9 61	2 21 2 9 6 2 0.8 76	1494 1485 1363 1200 1042.4 524.7 190 2245	2898.4 0.8 4.0 0.4 7.5 2.8 -5.6 1.8 2253.7	2918.9 0.7 2.6 9.9 8.8 9.0 -21.7 6.0 2255.7	2922.5 -1.0 3.2 11.0 8.1 8.7 -21.3 5.8 2255.5	δ_{s} CH ₂ , vCH δ_{s} CH ₃ , vBO δ_{as} CH ₃ , δ_{s} CH ₃ ρ CH ₃ ν CO δ OBO, δ BOC δ BOC, δ OBO ν CD ⁵ , ν_{s} CD ²
d ₉	v17 v18 v19 v20 v21 v22 v23 v15 v16	1534 1524 1393 1213 1071 530 197 2368 2206	1512 1498 1369 1194 042 522 173 2311 2166	1519 1502 1378 1200 1047 523 173 2307 2165	115 264 14 1167 30 156 25 9 61 117	2 21 2 9 6 2 0.8 76 0.6	1494 1485 1363 1200 1042.4 524.7 190 2245 2082	2898.4 0.8 4.0 0.4 7.5 2.8 -5.6 1.8 2253.7 2099.2	2918.9 0.7 2.6 9.9 8.8 9.0 -21.7 6.0 2255.7 2113.4	2922.5 -1.0 3.2 11.0 8.1 8.7 -21.3 5.8 2255.5 2116.1	v_{5} cH ₂ , vBO δ_{a} cH ₃ , vBO δ_{a} cH ₃ , δ_{5} cH ₃ ρ CH ₃ ρ CH ₃ ρ CH ₃ ρ CH ₃ ν CO δ 0BO, δ BOC δ 0BO, δ BOC δ 0BO, δ 0BO ν CD ⁵ , ν_{5} CD ² ₂ ν_{5} CD ² ₂ , ν CD ⁵
d9	V17 V18 V19 V20 V21 V22 V23 V15 V16 V17	1534 1524 1393 1213 1071 530 197 2368 2206 1426	1512 1498 1369 1194 042 522 173 2311 2166 1406	1519 1502 1378 1200 1047 523 173 2307 2165 1420	175 264 14 1167 30 156 25 9 61 117 1334	2 21 2 9 6 2 0.8 76 0.6 0.1	1494 1485 1363 1200 1042,4 524,7 190 2245 2082 1403	2898.4 0.8 4.0 0.4 7.5 2.8 -5.6 1.8 2253.7 2099.2 4.1	2918.9 0.7 2.6 9.9 8.8 9.0 -21.7 6.0 2255.7 2113.4 14.3 0.3	2922.5 -1.0 3.2 11.0 8.1 8.7 -21.3 5.8 2255.5 2116.1 14.3	v ₅ CH ₂ , vCH δ ₅ CH ₃ , vBO δ _a ₅ CH ₃ , δ ₅ CH ₃ vBO, δ ₅ CH ₃ νCO δOBO, δBOC δOBO, δBOC δBOC, δOBO vCD ⁵ , v ₅ CD ² v ₅ CD ² ₂ , vCD ⁵ vBO, δOBO
d9	 V17 V18 V19 V20 V21 V22 V23 V15 V16 V17 V18 	1534 1524 1393 1213 1071 530 197 2368 2206 1426 1161	1512 1498 1369 1194 042 522 173 2311 2166 1406 1135	1519 1502 1378 1200 1047 523 173 2307 2165 1420 1137 1005	175 264 14 1167 30 156 25 9 61 117 1334 192	2 21 2 9 6 2 0.8 76 0.6 0.1 1	1494 1485 1363 1200 1042.4 524.7 190 2245 2082 1403 1122.3	2898.4 0.8 4.0 0.4 7.5 2.8 -5.6 1.8 2253.7 2099.2 4.1 -3.2 4.1	2918.9 0.7 2.6 9.9 8.8 9.0 -21.7 6.0 2255.7 2113.4 14.3 0.6 2.2	2922.5 -1.0 3.2 11.0 8.1 8.7 -21.3 5.8 2255.5 2116.1 14.3 1.2 4.5	v ₅ CH ₂ , vCH δ ₃ CH ₃ , vBO δ ₃ cCH ₃ , δ ₅ CH ₃ vBO, δ ₅ CH ₃ vCO δOBO, δBOC δOBO, δBOC δBOC, δOBO vCD ⁵ , v ₅ CD ² v ₅ CD ² ₂ , vCD ⁵ vBO, δOBO δ ₅ CCD ₃ , vCO
d9	 V17 V18 V19 V20 V21 V22 V23 V15 V16 V17 V18 V19 V19 	1534 1524 1393 1213 1071 530 197 2368 2206 1426 1161 1099 1026	1512 1498 1369 1194 042 522 173 2311 2166 1406 1135 1081	1519 1502 1378 1200 1047 523 173 2307 2165 1420 1137 1085 1407	264 14 1167 30 156 25 9 61 117 1334 192 5 62	0.1 2 21 2 9 6 2 0.8 76 0.6 0.1 1 5 14	1494 1485 1363 1200 1042.4 524.7 190 2245 2082 1403 1122.3 1066 1001	2898.4 0.8 4.0 0.4 7.5 2.8 -5.6 1.8 2253.7 2099.2 4.1 -3.2 -1.5 0.8	2918.9 0.7 2.6 9.9 8.8 9.0 -21.7 6.0 2255.7 2113.4 14.3 0.6 -3.8 -3.8	2922.5 -1.0 3.2 11.0 8.1 8.7 -21.3 5.8 2255.5 2116.1 14.3 1.2 -4.5 -2.4	$v_5 CH_2$, VCH $\delta_5 CH_3$, VBO $\delta_{35} CH_3$, $\delta_5 CH_3$ ρCH_3 ρCH_3 νCO $\delta 0BO$, δBOC δBOC , $\delta 0BO$ νCD^5 , $v_5 CD_2^2$ $v_5 CD^3_2$, νCD^5 νBO , $\delta 0BO$ $\delta_5 CD_3$, νCO $\delta_{35} CD_3$ νCO
d9	V 17 V 18 V 19 V 20 V 21 V 22 V 23 V 15 V 16 V 17 V 18 V 19 V 20 V 20 V 20 V 20 V 20 V 20 V 20 V 21 V 21 V 22 V 23 V 21 V 20 V 21 V 20 V 20 V 21 V 20 V 20 V 20 V 21 V 20 V 20 V 20 V 20 V 20 V 20 V 20 V 20	1534 1524 1393 1213 1071 530 197 2368 2206 1426 1161 1099 1026 942	1512 1498 1369 1194 042 522 173 2311 2166 1406 1135 1081 1004 927	1519 1502 1378 1200 1047 523 173 2307 2165 1420 1137 1085 1007 930	264 14 1167 30 156 25 9 61 117 1334 192 5 63 17	2 21 2 9 6 2 0.8 76 0.6 0.1 1 5 14 3	1494 1485 1363 1200 1042.4 524.7 190 2245 2082 1403 1122.3 1066 1001 919	2898.4 0.8 4.0 0.4 7.5 2.8 -5.6 1.8 2253.7 2099.2 4.1 -3.2 -1.5 0.8 5.6	2918.9 0.7 2.6 9.9 8.8 9.0 -21.7 6.0 2255.7 2113.4 14.3 0.6 -3.8 -2.1 3.3	2922.5 -1.0 3.2 11.0 8.1 8.7 -21.3 5.8 2255.5 2116.1 14.3 1.2 -4.5 -2.4 2.9	v_{5} CH ₂ , vCH δ_{5} CH ₃ , vBO δ_{35} CH ₃ , δ_{5} CH ₃ ρ CH ₃ ν CO δ OBO, δ BOC δ BOC, δ OBO ν CD ⁵ , v_{5} CD ² v_{5} CD ² , ν CD ⁵ ν BO, δ OBO δ_{5} CD ₃ , ν CO δ_{45} CD ₅
d9	V17 V18 V19 V20 V21 V22 V23 V15 V16 V17 V18 V19 V20 V21 V22	1534 1524 1393 1213 1071 530 197 2368 2206 1426 1161 1099 1026 942 500	1512 1498 1369 1194 042 522 173 2311 2166 1406 1135 1081 1004 927 493	1519 1502 1378 1200 1047 523 173 2307 2165 1420 1137 1085 1007 930 494	264 14 1167 30 156 25 9 61 117 1334 192 5 63 17 18	0.1 2 21 2 9 6 2 0.8 76 0.6 0.1 1 5 14 3 2	1494 1485 1363 1200 1042.4 524.7 190 2245 2082 1403 1122.3 1066 1001 919 494	2898.4 0.8 4.0 0.4 7.5 2.8 -5.6 1.8 2253.7 2099.2 4.1 -3.2 -1.5 0.8 -5.6 -5.6	2918.9 0.7 2.6 9.9 8.8 9.0 -21.7 6.0 2255.7 2113.4 14.3 0.6 -3.8 -2.1 -3.3 -19.7	2922.5 -1.0 3.2 11.0 8.1 8.7 -21.3 5.8 2255.5 2116.1 14.3 1.2 -4.5 -2.4 -2.9 -19.4	v_{5} CH ₂ , vEO δ_{3} CH ₃ , vBO δ_{a} CH ₃ , δ_{5} CH ₃ ρ CH ₃ ρ CH ₃ ρ CH ₃ ρ CC δ OBO, δ BOC δ BOC, δ OBO ν CD ⁵ , v_{5} CD ² v_{5} CD ² ₂ , ν CD ⁵ ν BO, δ OBO δ_{5} CD ₃ , ν CO ρ CD ₃ δ OBO, δ BOC
d9	 V18 V19 V20 V21 V22 V23 V15 V16 V17 V18 V19 V20 V21 V22 V22 V22 V22 V21 V22 V22 V22 V22 V22 V22 V23 V21 V22 V22 V22 V22 V22 V23 V21 V22 V22 V23 V23 V21 V22 V23 V23 V23 V23 V23 V24 V25 V23 V24 V25 V25 V25 V26 V26 V27 V26 V27 V27	1534 1524 1393 1213 1071 530 197 2368 2206 1426 1161 1099 1026 942 500 166	1512 1498 1369 1194 042 522 173 2311 2166 1406 1135 1081 1004 927 493 153	1519 1502 1378 1200 1047 523 173 2307 2165 1420 1137 1085 1007 930 494 153	264 14 1167 30 156 25 9 61 117 1334 192 5 63 17 18 7	0.1 2 21 2 9 6 2 0.8 76 0.6 0.1 1 5 14 3 2 06	1494 1485 1363 1200 1042.4 524.7 190 2245 2082 1403 1122.3 1066 1001 919 494 168	$\begin{array}{c} 2898.4\\ 0.8\\ 4.0\\ 0.4\\ 7.5\\ 2.8\\ -5.6\\ 1.8\\ 2253.7\\ 2099.2\\ 4.1\\ -3.2\\ -1.5\\ 0.8\\ -5.6\\ -5.6\\ 1.3\end{array}$	2918.9 0.7 2.6 9.9 8.8 9.0 -21.7 6.0 2255.7 2113.4 14.3 0.6 -3.8 -2.1 -3.3 -19.7 5.3	2922.5 -1.0 3.2 11.0 8.1 8.7 -21.3 5.8 2255.5 2116.1 14.3 1.2 -4.5 -2.4 -2.9 -19.4 5 1	$v_5 CH_2$, vEN $\delta_5 CH_3$, vBO $\delta_{a5} CH_3$, $\delta_5 CH_3$ ρCH_3 νCO δOBO , δBOC δOBO , δBOC δBOC , δOBO νCD^5 , $v_5 CD_2^3$ $v_5 CD^3_2$, νCD^5 νBO , δOBO $\delta_{a5} CD_3$, νCO $\delta_{a5} CD_3$ νCO ρCD_3 δOBO , δBOC δBOC , δOBO
d9 Species	V18 V19 V20 V21 V22 V23 V15 V16 V17 V18 V19 V20 V21 V22 V23 Mode	1534 1524 1393 1213 1071 530 197 2368 2206 1426 1161 1099 1026 942 500 166 	1512 1498 1369 1194 042 522 173 2311 2166 1406 1135 1081 1004 927 493 153	1519 1502 1378 1200 1047 523 173 2307 2165 1420 1137 1085 1007 930 494 153	264 14 1167 30 156 25 9 61 117 1334 192 5 63 17 18 7 7	0.1 2 21 2 9 6 2 0.8 76 0.6 0.1 1 5 14 3 2 0.6 <i>R</i> .(rg. ^b	1494 1485 1363 1200 1042,4 524,7 190 2245 2082 1403 1122,3 1066 1001 919 494 168 voted S	2898.4 0.8 4.0 0.4 7.5 2.8 -5.6 1.8 2253.7 2099.2 4.1 -3.2 -1.5 0.8 -5.6 1.3 Vmrz4 ^d	$\begin{array}{c} 2918.9\\ 0.7\\ 2.6\\ 9.9\\ 8.8\\ 9.0\\ -21.7\\ 6.0\\ 2255.7\\ 2113.4\\ 14.3\\ 0.6\\ -3.8\\ -2.1\\ -3.3\\ -19.7\\ 5.3\\ v_{dtyt}^{d}\end{array}$	2922.5 -1.0 3.2 11.0 8.1 8.7 -21.3 5.8 2255.5 2116.1 14.3 1.2 -4.5 -2.4 -2.9 -19.4 5.1 <i>Vacor</i> ^d	k_{5} CH ₂ , vCH δ_{5} CH ₃ , vBO δ_{a5} CH ₃ , δ_{5} CH ₃ ρ CH ₃ ρ CH ₃ ν CO δ OBO, δ BOC δ OBO, δ BOC δ BOC, δ OBO ν CD ⁵ , ν_{5} CD ² ν_{5} CD ² ₂ , ν CD ⁵ ν BO, δ OBO δ_{a5} CD ₃ ν CO ρ CD ₃ δ OBO, δ BOC δ BOC, δ OBO Motion
d ₉ Species	V18 V19 V20 V21 V22 V23 V15 V16 V17 V18 V19 V20 V21 V22 V23 Mode	1534 1524 1393 1213 1071 530 197 2368 2206 1426 1426 1426 1426 1426 1426 1426 1099 1026 942 500 166 <i>ω</i> _{mtz+} ^a	$\begin{array}{c} 1512\\ 1498\\ 1369\\ 1194\\ 042\\ 522\\ 173\\ 2311\\ 2166\\ 1406\\ 1135\\ 1081\\ 1004\\ 927\\ 493\\ 153\\ \\ \varpi_{dtz*}{}^{a} \end{array}$	3521 1519 1502 1378 1200 1047 523 173 2307 2165 1420 1137 1085 1007 930 494 153	264 14 1167 30 156 25 9 61 117 1334 192 5 63 17 18 7 7 xact ^a	0.1 2 21 2 9 6 2 0.8 76 0.6 0.1 1 5 14 3 2 0.6 6 R _{dtz*} ^b	$\begin{array}{c} 1494\\ 1485\\ 1363\\ 1200\\ 1042.4\\ 524.7\\ 190\\ 2245\\ 2082\\ 1403\\ 1122.3\\ 1066\\ 1001\\ 919\\ 494\\ 168\\ v_{obsd} \\ c\end{array}$	2898.4 0.8 4.0 0.4 7.5 2.8 -5.6 1.8 2253.7 2099.2 4.1 -3.2 -1.5 0.8 -5.6 1.3 v _{mtz*} ^d	2918.9 0.7 2.6 9.9 8.8 9.0 -21.7 6.0 2255.7 2113.4 14.3 0.6 -3.8 -2.1 -3.3 -19.7 5.3 v _{dtz*} ^d	2922.5 -1.0 3.2 11.0 8.1 8.7 -21.3 5.8 2255.5 2116.1 14.3 1.2 -4.5 -2.4 -2.9 -19.4 5.1 vdcct ^d	k_{S} CH ₂ , vEN δ_{S} CH ₃ , vBO δ_{aS} CH ₃ , δ_{S} CH ₃ ν BO, δ_{S} CH ₃ ρ CH ₃ ν CO δ OBO, δ BOC δ OBO, δ BOC δ OBO, δ OBO ν CD ⁵ , ν_{S} CD ² ν_{S} CD ² , ν CD ⁵ ν BO, δ OBO δ_{S} CD ₃ , ν CO ρ CD ₃ δ OBO, δ BOC δ BOC, δ OBO Motion
d ₉ Species	V17 V18 V19 V20 V21 V22 V23 V15 V16 V17 V18 V19 V20 V21 V22 V23 Mode	1534 1524 1393 1213 1071 530 197 2368 2206 1426 1161 1099 1026 942 500 166 ω_{mtz*}^{a}	$\begin{array}{c} 1512 \\ 1498 \\ 1369 \\ 1194 \\ 042 \\ 522 \\ 173 \\ 2311 \\ 2166 \\ 1406 \\ 1135 \\ 1081 \\ 1004 \\ 927 \\ 493 \\ 153 \\ \varpi_{dtz+}{}^{a} \end{array}$	3521 1519 1502 1378 1200 1047 523 173 2307 2165 1420 1137 1085 1007 930 494 153	264 14 1167 30 156 25 9 61 117 1334 192 5 63 17 18 7 7 282	$ \begin{array}{c} 0.1 \\ 2 \\ 2 \\ 2 \\ 9 \\ 6 \\ 2 \\ 0.8 \\ 76 \\ 0.6 \\ 0.1 \\ 1 \\ 5 \\ 14 \\ 3 \\ 2 \\ 0.6 \\ R_{dtz^{+}}^{b} \\ 171 \end{array} $	1494 1485 1363 1200 1042.4 524.7 190 2245 2082 1403 1122.3 1066 1001 919 494 168 v _{obsd} ^c	2898.4 0.8 4.0 0.4 7.5 2.8 -5.6 1.8 2253.7 2099.2 4.1 -3.2 -1.5 0.8 -5.6 -5.6 1.3 v _{mtz+} ^d	2918.9 0.7 2.6 9.9 8.8 9.0 -21.7 6.0 2255.7 2113.4 14.3 0.6 -3.8 -2.1 -3.3 -19.7 5.3 v _{dtz+} ^d	2922.5 -1.0 3.2 11.0 8.1 8.7 -21.3 5.8 2255.5 2116.1 14.3 1.2 -4.5 -2.4 -2.9 -19.4 5.1 $v_{\rm dect}^{\rm d}$	$\rho_{S}CH_{2}, \nu CH$ $\delta_{S}CH_{3}, \nu BO$ $\delta_{aS}CH_{3}, \delta_{S}CH_{3}$ $\rho CH_{3}, \delta_{S}CH_{3}$ ρCH_{3} νCO $\delta OBO, \delta BOC$ $\delta OBO, \delta BOC$ $\delta OBO, \delta OBO$ $\nu CD^{S}, \nu_{S}CD^{2}$ $\nu_{S}CD^{2}_{2}, \nu CD^{S}$ $\nu BO, \delta OBO$ $\delta_{S}CD_{3}, \nu CO$ $\delta_{aS}CD_{3}$ νCO ρCD_{3} $\delta OBO, \delta BOC$ $\delta BOC, \delta OBO$ Motion
d ₉ Species E'' d ₀	V17 V18 V19 V20 V21 V22 V23 V15 V16 V17 V18 V19 V20 V21 V22 V23 Mode	$1534 \\ 1524 \\ 1393 \\ 1213 \\ 1071 \\ 530 \\ 197 \\ 2368 \\ 2206 \\ 1426 \\ 1161 \\ 1099 \\ 1026 \\ 942 \\ 500 \\ 166 \\ \omega_{\text{mtz*}^{4}} \\ 3166 \\ 1515 \\ \end{cases}$	$\begin{array}{c} 1512\\ 1498\\ 1369\\ 1194\\ 042\\ 522\\ 173\\ 2311\\ 2166\\ 1406\\ 1135\\ 1081\\ 1004\\ 927\\ 493\\ 153\\ \\ \omega_{dtz*}{}^a\\ \end{array}$	3021 1519 1502 1378 1200 1047 523 173 2307 2165 1420 1137 1085 1007 930 494 153	264 14 1167 30 156 25 9 61 117 1334 192 5 63 17 18 7 18 7 882 98	$ \begin{array}{c} 0.1 \\ 2 \\ 2 \\ $	1494 1485 1363 1200 1042.4 524.7 190 2245 2082 1403 1122.3 1066 1001 919 494 168 v _{obsd} ^c	2898.4 0.8 4.0 0.4 7.5 2.8 -5.6 1.8 2253.7 2099.2 4.1 -3.2 -1.5 0.8 -5.6 1.3 v _{mtz+} ^d 2979.7 1477.4	$\begin{array}{c} 2918.9\\ 0.7\\ 2.6\\ 9.9\\ 8.8\\ 9.0\\ -21.7\\ 6.0\\ 2255.7\\ 2113.4\\ 14.3\\ 0.6\\ -3.8\\ -2.1\\ -3.3\\ -19.7\\ 5.3\\ v_{dtz*}^{d}\end{array}$	2922.5 -1.0 3.2 11.0 8.1 8.7 -21.3 5.8 2255.5 2116.1 14.3 1.2 -4.5 -2.4 -2.9 -19.4 5.1 v _{decet} ^d	v_{5} CH ₂ , vCH δ_{3} CH ₃ , vBO δ_{3} CH ₃ , δ_{5} CH ₃ ν BO, δ_{5} CH ₃ ρ CH ₃ ν CO δ OBO, δ BOC δ BOC, δ OBO ν CD ⁵ , v_{5} CD ² ν_{5} CD ² , ν CD ⁵ ν BO, δ OBO δ_{5} CD ₃ , ν CO δ_{6} CD ₃ δ OBO, δ BOC δ BOC, δ OBO Motion ν_{as} CH ₃ δ_{5} CH ₂
d ₉ Species E″ d ₀	V17 V18 V19 V20 V21 V22 V23 V15 V16 V17 V18 V19 V20 V21 V22 V23 Mode	1534 1524 1393 1213 1071 530 197 2368 2206 1426 1161 1099 1026 942 500 166 <i>ω</i> _{mtz+} ^a 3166 1515 1200	1512 1498 1369 1194 042 522 173 2311 2166 1406 1135 1081 1004 927 493 153 Ødtz+ ^a 3088 1495 1177	3521 1519 1502 1378 1200 1047 523 173 2307 2165 1420 1137 1085 1007 930 494 153 00 1420	264 14 1167 30 156 25 9 61 117 1334 192 5 63 17 18 7 4cct ³	0.1 2 21 2 9 6 2 0.8 76 0.6 0.1 1 5 14 3 2 0.6 $R_{dtz^+}^{b}$ 171 32 8	1494 1485 1363 1200 1042.4 524.7 190 2245 2082 1403 1122.3 1066 1001 919 494 168 vobsd ^c	2898.4 0.8 4.0 0.4 7.5 2.8 -5.6 1.8 2253.7 2099.2 4.1 -3.2 -1.5 0.8 -5.6 -5.6 1.3 $v_{mtz^{+}}$ 2979.7 1477.4 1177.4	$\begin{array}{c} 2918.9\\ 0.7\\ 2.6\\ 9.9\\ 8.8\\ 9.0\\ -21.7\\ 6.0\\ 2255.7\\ 2113.4\\ 14.3\\ 0.6\\ -3.8\\ -2.1\\ -3.3\\ -19.7\\ 5.3\\ v_{dtz*}^{\rm d}\\ \end{array}$	2922.5 -1.0 3.2 11.0 8.1 8.7 -21.3 5.8 2255.5 2116.1 14.3 1.2 -4.5 -2.4 -2.9 -19.4 5.1 <i>v</i> dcct ^d 2979.5 1475.7 1472.3	v_{5} CH ₂ , vBO δ_{a5} CH ₃ , vBO δ_{a5} CH ₃ , δ_{5} CH ₃ ρ CH ₃ ρ CH ₃ ρ CH ₃ ν CO δ BOC, δ BOC δ BOC, δ BOC δ BOC, δ CD ν CD ⁵ , ν_{5} CD ² ν_{5} CD ² ₂ , ν CD ⁵ ν BO, δ OBO δ_{5} CD ₃ , ν CO δ OBO, δ BOC δ BOC, δ CD δ OBO, δ CH ₃ δ_{a5} CH ₃ δ_{a5} CH ₃
d ₉ Species E'' d ₀	V17 V18 V19 V20 V21 V22 V23 V15 V16 V17 V18 V19 V20 V21 V22 V23 Mode V24 V25 V26 V27	1534 1524 1393 1213 1071 530 197 2368 2206 1426 1161 1099 1026 942 500 166 <i>ω</i> _{mtz+} ^a 3166 1515 1200 175	$\begin{array}{c} 1512\\ 1498\\ 1369\\ 1194\\ 042\\ 522\\ 173\\ 2311\\ 2166\\ 1406\\ 1135\\ 1081\\ 1004\\ 927\\ 493\\ 153\\ \\ & \varpi_{dtz*}^{a}\\ \end{array}$	3521 1519 1502 1378 1200 1047 523 173 2307 2165 1420 1137 1085 1007 930 494 153 ωα 30 14 11 18	264 14 1167 30 156 25 9 61 117 1334 192 5 63 17 18 7 4cct ³	171 32 0,6 2 0,8 76 0,6 0,1 1 5 14 3 2 0,6 R _{dtz+} ^b 171 32 8 0,2	1494 1485 1363 1200 1042.4 524.7 190 2245 2082 1403 1122.3 1066 1001 919 494 168 v _{obsd} ^c	2898.4 0.8 4.0 0.4 7.5 2.8 -5.6 1.8 2253.7 2099.2 4.1 -3.2 -1.5 0.8 -5.6 1.3 v _{mtz+} ^d 2979.7 1477.4 179.7	$\begin{array}{c} 2918.9\\ 0.7\\ 2.6\\ 9.9\\ 8.8\\ 9.0\\ -21.7\\ 6.0\\ 2255.7\\ 2113.4\\ 14.3\\ 0.6\\ -3.8\\ -2.1\\ -3.3\\ -19.7\\ 5.3\\ \nu_{dtz*}^{d}\\ \end{array}$	2922.5 -1.0 3.2 11.0 8.1 8.7 -21.3 5.8 2255.5 2116.1 14.3 1.2 -4.5 -2.4 -2.9 -19.4 5.1 v_{dect}^{d} 2979.5 1475.7 1174.3 175.8	v_{5} CH ₂ , vBO δ_{a5} CH ₃ , vBO δ_{a5} CH ₃ , δ_{5} CH ₃ ρ CH ₃ ρ CH ₃ ν CO δ OBO, δ BOC δ BOC, δ OBO ν CD ⁵ , ν_{5} CD ² ν_{5} CD ² , ν CD ⁵ ν BO, δ OBO δ_{5} CD ₃ , ν CO δ_{a5} CD ₃ ν CO ρ CD ₃ δ OBO, δ BOC δ BOC, δ OBO δ BOC, δ OBO δ Motion ν_{a5} CH ₃ δ_{a5} CH ₃ ρ CH ₃ δ_{a5} CH ₃ ρ CH ₃ δ_{a5} CH ₃ ρ CH ₃
d ₉ Species E'' d ₀	V17 V18 V19 V20 V21 V22 V23 V15 V16 V17 V18 V19 V20 V21 V22 V23 Mode V24 V25 V26 V27 V22 V23	$\begin{array}{c} 1534\\ 1524\\ 1393\\ 1213\\ 1071\\ 530\\ 197\\ 2368\\ 2206\\ 1426\\ 1426\\ 1426\\ 1426\\ 1426\\ 1099\\ 1026\\ 942\\ 500\\ 166\\ 0_{\text{mtz}*}^{a}\\ 3166\\ 1515\\ 1200\\ 175\\ 55\end{array}$	$\begin{array}{c} 1512\\ 1498\\ 1369\\ 1194\\ 042\\ 522\\ 173\\ 2311\\ 2166\\ 1406\\ 1135\\ 1081\\ 1004\\ 927\\ 493\\ 153\\ \hline $$ $$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$	302 1 1519 1502 1378 1200 1047 523 173 2307 2165 1420 1137 1085 1007 930 494 153 00 14 11 18 60	264 14 1167 30 156 25 9 61 117 1334 192 5 63 17 18 7 7 18 7 82 .98 84 5 5	$ \begin{array}{c} \text{0.1} \\ \text{2} \\ \text{21} \\ \text{2} \\ \text{9} \\ \text{6} \\ \text{2} \\ \text{0.8} \\ \text{76} \\ \text{0.6} \\ \text{0.1} \\ \text{1} \\ \text{5} \\ \text{14} \\ \text{3} \\ \text{2} \\ \text{0.6} \\ \text{R}_{\text{dtz}^{\text{b}}} \\ \text{171} \\ \text{32} \\ \text{8} \\ \text{0.2} \\ \text{0.7} \\ \end{array} $	1494 1485 1363 1200 1042,4 524,7 190 2245 2082 1403 1122,3 1066 1001 919 494 168 vobsd ^c	2898.4 0.8 4.0 0.4 7.5 2.8 -5.6 1.8 2253.7 2099.2 4.1 -3.2 -1.5 0.8 -5.6 1.3 v_{mtz*}^{d} 2979.7 1477.4 1177.4 1177.7 65 9	$\begin{array}{c} 2918.9\\ 0.7\\ 2.6\\ 9.9\\ 8.8\\ 9.0\\ -21.7\\ 6.0\\ 2255.7\\ 2113.4\\ 14.3\\ 0.6\\ -3.8\\ -2.1\\ -3.8\\ -2.1\\ -3.3\\ -19.7\\ 5.3\\ v_{dtz^{+}}^{d}\\ \end{array}$	2922.5 -1.0 3.2 11.0 8.1 8.7 -21.3 5.8 2255.5 2116.1 14.3 1.2 -4.5 -2.4 -2.9 -19.4 5.1 v_{dect} 2979.5 1475.7 1174.3 175.8 49 1	v_{5} CH ₂ , vEO δ_{5} CH ₃ , vBO δ_{a5} CH ₃ , δ_{5} CH ₃ ρ CH ₃ ρ CH ₃ ν CO δ OBO, δ BOC δ OBO, δ BOC δ OBO, δ OBO ν CD ⁵ , v_{5} CD ² ν_{5} CD ² ₂ , ν CD ⁵ ν BO, δ OBO δ_{5} CD ₃ , ν CO δ_{a5} CD ₃ ν CO ρ CD ₃ δ OBO, δ BOC δ BOC, δ OBO Motion v_{a5} CH ₃ ρ CH ₃ τ OBO τ CH ₂
d ₉ Species E″ d ₀	V17 V18 V19 V20 V21 V22 V23 V15 V16 V17 V18 V19 V20 V21 V22 V23 Mode V24 V25 V26 V27 V28	$1534 \\ 1524 \\ 1393 \\ 1213 \\ 1071 \\ 530 \\ 197 \\ 2368 \\ 2206 \\ 1426 \\ 1161 \\ 1099 \\ 1026 \\ 942 \\ 500 \\ 166 \\ \varpi_{mtz*}^{a} \\ 3166 \\ 1515 \\ 1200 \\ 175 \\ 55 \\ 1200 \\ 100 \\$	$\begin{array}{c} 1512\\ 1498\\ 1369\\ 1194\\ 042\\ 522\\ 173\\ 2311\\ 2166\\ 1406\\ 1135\\ 1081\\ 1004\\ 927\\ 493\\ 153\\ \\ & \varpi_{dtz*}^{a}\\ \end{array}$	$\begin{array}{c} 5521\\ 1519\\ 1502\\ 1378\\ 1200\\ 1047\\ 523\\ 173\\ 2307\\ 2165\\ 1420\\ 1137\\ 1085\\ 1007\\ 930\\ 494\\ 153\\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	264 14 1167 30 156 25 9 61 117 1334 192 5 63 17 18 7 7 63 17 18 7 82 98 84 5	1711 2 2 2 2 2 9 6 2 0.8 76 0.6 0.1 1 5 14 3 2 0.6 R _{dtz*} ^b 171	1494 1485 1363 1200 1042.4 524.7 190 2245 2082 1403 1122.3 1066 1001 919 494 168 v _{obsd} ^c	2898.4 0.8 4.0 0.4 7.5 2.8 -5.6 1.8 2253.7 2099.2 4.1 -3.2 -1.5 0.8 -5.6 -5.6 1.3 $v_{mtz^{+}}$ 2979.7 1477.4 1177.4 179.7 65.9	$\begin{array}{c} 2918.9\\ 0.7\\ 2.6\\ 9.9\\ 8.8\\ 9.0\\ -21.7\\ 6.0\\ 2255.7\\ 2113.4\\ 14.3\\ 0.6\\ -3.8\\ -2.1\\ -3.3\\ -19.7\\ 5.3\\ v_{dtz*}^{4}\\ \end{array}$	$2922.5 \\ -1.0 \\ 3.2 \\ 11.0 \\ 8.1 \\ 8.7 \\ -21.3 \\ 5.8 \\ 2255.5 \\ 2116.1 \\ 14.3 \\ 1.2 \\ -4.5 \\ -2.4 \\ -2.9 \\ -19.4 \\ 5.1 \\ v_{dect}^{d} \\ 2979.5 \\ 1475.7 \\ 1174.3 \\ 175.8 \\ 49.1 \\ 1000$	$\begin{array}{c} v_{5} {\rm CH}_{2}, {\rm VEO} \\ \delta_{3} {\rm CH}_{3}, {\rm vBO} \\ \delta_{3} {\rm CH}_{3}, {\rm vBO}, \delta_{3} {\rm CH}_{3} \\ {\rm vBO}, \delta_{3} {\rm CH}_{3}, \delta_{5} {\rm CH}_{3} \\ {\rm vCO} \\ \delta {\rm OBO}, \delta {\rm BOC} \\ \delta {\rm OBO}, \delta {\rm BOC} \\ \delta {\rm OBO}, \delta {\rm ABOC} \\ \delta {\rm CD}_{3}, {\rm vCD}^{3} \\ {\rm v}_{5} {\rm CD}_{2}, {\rm vCD}^{5} \\ {\rm vBO}, \delta {\rm OBO} \\ \delta_{5} {\rm CD}_{3}, {\rm vCO} \\ \delta_{3} {\rm cCD} \\ \delta {\rm CD}, \delta {\rm OBO} \\ \delta {\rm OBO}, \delta {\rm BOC} \\ \delta {\rm OBO}, \delta {\rm BOC} \\ \delta {\rm BOC}, \delta {\rm OBO} \\ \hline \\ {\rm vasCH}_{3} \\ \delta_{4} {\rm cCH}_{3} \\ {\rm rOBOC} \\ {\rm rCH}_{3} \\ {\rm rOBOC} \\ {\rm rCH}_{3} \\ \end{array}$
d ₉ Species E ⁿ d ₀	V17 V18 V19 V20 V21 V22 V23 V15 V16 V17 V18 V19 V20 V21 V22 V23 Mode V24 V25 V26 V27 V28	$\begin{array}{c} 1534\\ 1524\\ 1393\\ 1213\\ 1071\\ 530\\ 197\\ 2368\\ 2206\\ 1426\\ 1161\\ 1099\\ 1026\\ 942\\ 500\\ 166\\ & \varpi_{\mathrm{mtz*}^{a}}^{a} \end{array}$	$\begin{array}{c} 1512\\ 1498\\ 1369\\ 1194\\ 042\\ 522\\ 173\\ 2311\\ 2166\\ 1406\\ 1135\\ 1081\\ 1004\\ 927\\ 493\\ 153\\ \\ \hline \ $	3021 1519 1502 1378 1200 1047 523 173 2307 2165 1420 1137 1085 1007 930 494 153 00 14 18 60	264 14 1167 30 156 25 9 61 117 1334 192 5 63 17 18 7 18 7 82 98 84 5	$\begin{array}{c} 0.1\\ 2\\ 21\\ 2\\ 9\\ 6\\ 2\\ 0.8\\ 76\\ 0.6\\ 0.1\\ 1\\ 5\\ 14\\ 3\\ 2\\ 0.6\\ R_{dtz^+}{}^{b}\\ 171\\ 32\\ 8\\ 0.2\\ 0.7\\ 00\\ \end{array}$	1494 1485 1363 1200 1042.4 524.7 190 2245 2082 1403 1122.3 1066 1001 919 494 168 v _{obsd} ^c	2898.4 0.8 4.0 0.4 7.5 2.8 -5.6 1.8 2253.7 2099.2 4.1 -3.2 -1.5 0.8 -5.6 -5.6 1.3 v_{mtz*}^{d} 2979.7 1477.4 177.4 179.7 65.9	$\begin{array}{c} 2918.9\\ 0.7\\ 2.6\\ 9.9\\ 8.8\\ 9.0\\ -21.7\\ 6.0\\ 2255.7\\ 2113.4\\ 14.3\\ 0.6\\ -3.8\\ -2.1\\ -3.3\\ -19.7\\ 5.3\\ v_{dtz*}^{\rm d}\\ \end{array}$	$\begin{array}{c} 2922.5 \\ -1.0 \\ 3.2 \\ 11.0 \\ 8.1 \\ 8.7 \\ -21.3 \\ 5.8 \\ 2255.5 \\ 2116.1 \\ 14.3 \\ 1.2 \\ -4.5 \\ -2.4 \\ -2.9 \\ -19.4 \\ 5.1 \\ v_{dect} \\ \end{array}$	v_{3} CH ₂ , vCH δ_{3} CH ₃ , vBO δ_{3} CH ₃ , δ_{5} CH ₃ ρ CH ₃ ν BO, δ_{5} CH ₃ ρ CH ₃ ν CO δ OBO, δ BOC δ OBO, δ BOC δ OBO, δ OBO ν CD ⁵ , v_{5} CD ² ν_{5} CD ² , ν_{5} CD ² ν_{5} CD ² , ν_{5} CD ³ ν_{5} CD ³ , ν_{7} CO δ_{45} CD ₃ , ν CO δ_{65} CD ₃ , ν CO ρ CD ₃ δ OBO, δ BOC δ OBO, δ BOC δ OBO Motion ν_{a5} CH ₃ ρ CH ₃ τ OBOC τ CH ₃ ν_{5} CD
d ₉ Species E'' d ₀ d ₉	V17 V18 V19 V20 V21 V22 V23 V15 V16 V17 V18 V19 V20 V21 V22 V23 Mode V21 V22 V23 Mode	$1534 \\ 1524 \\ 1393 \\ 1213 \\ 1071 \\ 530 \\ 197 \\ 2368 \\ 2206 \\ 1426 \\ 1161 \\ 1099 \\ 1026 \\ 942 \\ 500 \\ 166 \\ \varpi_{mtz*}^{a} \\ 3166 \\ 1515 \\ 1200 \\ 175 \\ 55 \\ 2350 \\ 1005 \\ $	$\begin{array}{c} 1512\\ 1498\\ 1369\\ 1194\\ 042\\ 522\\ 173\\ 2311\\ 2166\\ 1406\\ 1135\\ 1081\\ 1004\\ 927\\ 493\\ 153\\ & \omega_{dtz*}^a\\ \\ 3088\\ 1495\\ 1177\\ 183\\ 53\\ \\ 2291\\ 1090\\ \end{array}$	3521 1519 1502 1378 1200 1047 523 173 2307 2165 1420 1137 1085 1007 930 494 153 30 141 18 60 22 10	264 14 1167 30 156 25 9 61 117 1334 192 5 63 17 18 7 18 7 82 98 84 5 5	$\begin{array}{c} 0.1\\ 2\\ 2\\ 1\\ 2\\ 9\\ 6\\ 2\\ 0.8\\ 76\\ 0.6\\ 0.1\\ 1\\ 5\\ 14\\ 3\\ 2\\ 0.6\\ R_{dtz^+}{}^{b}\\ \end{array}$	1494 1485 1363 1200 1042.4 524.7 190 2245 2082 1403 1122.3 1066 1001 919 494 168 v _{obsd} ^c	2898.4 0.8 4.0 0.4 7.5 2.8 -5.6 1.8 2253.7 2099.2 4.1 -3.2 -1.5 0.8 -5.6 -5.6 1.3 v_{mtz*}^{d} 2979.7 1477.4 177.4 177.7 65.9 2236.5 1067.0	$\begin{array}{c} 2918.9\\ 0.7\\ 2.6\\ 9.9\\ 8.8\\ 9.0\\ -21.7\\ 6.0\\ 2255.7\\ 2113.4\\ 14.3\\ 0.6\\ -3.8\\ -2.1\\ -3.3\\ -19.7\\ 5.3\\ v_{dtz*}^{\rm d}\\ \end{array}$	2922.5 -1.0 3.2 11.0 8.1 8.7 -21.3 5.8 2255.5 2116.1 14.3 1.2 -4.5 -2.4 -2.9 -19.4 5.1 vdcct ^d 2979.5 1475.7 1174.3 175.8 49.1 2235.6	v_{3} CH ₃ , vBO δ_{3} CH ₃ , vBO δ_{3} CH ₃ , δ_{5} CH ₃ ρ CH ₃ ρ CH ₃ ρ CH ₃ ν CO δ OBO, δ BOC δ BOC, δ OBO ν CD ⁵ , ν_{5} CD ² ν_{5} CD ² ₂ , ν CD ⁵ ν BO, δ OBO δ_{5} CD ₃ , ν CO δ_{2} CD ₃ , ν CO δ OBO, δ BOC δ BOC, δ OBO Motion v_{as} CH ₃ τ OBOC τ CH ₃ τ OBOC τ CH ₃ τ OBOC τ CH ₃ τ CD
d9 Species E″ d0	V17 V18 V19 V20 V21 V22 V23 V15 V16 V17 V18 V19 V20 V21 V22 V23 Mode V24 V25 V26 V27 V28 V24 V22 V28	1534 1524 1393 1213 1071 530 197 2368 2206 1426 1161 1099 1026 942 500 166 ω_{mtz*}^{a} 3166 1515 1200 175 55 2350 1095 927	$\begin{array}{c} 1512\\ 1498\\ 1369\\ 1194\\ 042\\ 522\\ 173\\ 2311\\ 2166\\ 1406\\ 1135\\ 1081\\ 1004\\ 927\\ 493\\ 153\\ \\ & \varpi_{dtz*}^{a}\\ \end{array}$	3521 1519 1502 1378 1200 1047 523 173 2307 2165 1420 1137 1085 1007 930 494 153 ∞α 300 14 11 18 60 22 10	264 14 1167 30 156 25 9 61 117 1334 192 5 63 17 18 7 steet ^a 82 98 84 5 5 87 83 5	0.1 2 2 2 9 6 2 0.8 76 0.6 0.1 1 5 14 3 2 0.6 R _{dtz+} ^b 171 32 8 0.2 0.7 90 12 8	1494 1485 1363 1200 1042.4 524.7 190 2245 2082 1403 1122.3 1066 1001 919 494 168 v _{obsd} ^c	2898.4 0.8 4.0 0.4 7.5 2.8 -5.6 1.8 2253.7 2099.2 4.1 -3.2 -1.5 0.8 -5.6 -5.6 1.3 vmtz* ^d 2979.7 1477.4 1177.4 1177.4 179.7 65.9 2236.5 1067.0 910.2	$\begin{array}{c} 2918.9\\ 0.7\\ 2.6\\ 9.9\\ 8.8\\ 9.0\\ -21.7\\ 6.0\\ 2255.7\\ 2113.4\\ 14.3\\ 0.6\\ -3.8\\ -2.1\\ -3.3\\ -19.7\\ 5.3\\ v_{dtz*}^{d}\\ \end{array}$	$\begin{array}{c} 2922.5 \\ -1.0 \\ 3.2 \\ 11.0 \\ 8.1 \\ 8.7 \\ -21.3 \\ 5.8 \\ 2255.5 \\ 2116.1 \\ 14.3 \\ 1.2 \\ -4.5 \\ -2.4 \\ -2.9 \\ -19.4 \\ 5.1 \\ v_{dect}{}^{d} \\ \end{array}$	v_{3} CH ₃ , vBO δ_{a} CH ₃ , vBO δ_{a} CH ₃ , δ_{5} CH ₃ ρ CH ₃ ρ CH ₃ ρ CH ₃ ρ CH ₃ ρ CC δ DBO, δ BOC δ BOC, δ OBO ν CD ⁵ , v_{5} CD ² v_{5} CD ² , ν CD ⁵ ν BO, δ OBO δ_{5} CD ₃ ν CO ρ CD ₃ δ OBO, δ BOC δ BOC, δ OBO Motion v_{as} CH ₃ δ_{as} CH ₃ ρ CH ₃ τ OBOC τ CH ₃ σ CD ₃ δ_{as} CD ₃ δ CD ₃ δ CD ₃
d ₉ Species E'' d ₀	V17 V18 V19 V20 V21 V22 V23 V15 V16 V17 V18 V19 V20 V21 V22 V23 Mode V24 V25 V26 V27 V28 V24 V25 V26 V27 V28	1534 1524 1393 1213 1071 530 197 2368 2206 1426 1161 1099 1026 942 500 166 1515 1200 175 55 2350 1095 927 162	$\begin{array}{c} 1512\\ 1498\\ 1369\\ 1194\\ 042\\ 522\\ 173\\ 2311\\ 2166\\ 1406\\ 1135\\ 1081\\ 1004\\ 927\\ 493\\ 153\\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	302 1 1519 1502 1378 1200 1047 523 173 2307 2165 1420 1137 1085 1007 930 494 153 00 14 18 60 22 10 91 12	264 14 1167 30 156 25 9 61 117 1334 192 5 63 17 18 7 4 82 98 84 5 6 87 83 5 0	 0.1 2 21 2 9 6 2 0.8 76 0.6 0.1 1 1 5 14 3 2 0.6 <i>R</i>_{dtz+}^b 171 32 8 0.2 0.7 90 12 8 0.3 	1494 1485 1363 1200 1042.4 524.7 190 2245 2082 1403 1122.3 1066 1001 919 494 168 vobsd ^c	2898.4 0.8 4.0 0.4 7.5 2.8 -5.6 1.8 2253.7 2099.2 4.1 -3.2 -1.5 0.8 -5.6 1.3 v_{mtz*}^{d} 2979.7 1477.4 1177.4 179.7 65.9 2236.5 1067.0 910.2 166 5	$\begin{array}{c} 2918.9\\ 0.7\\ 2.6\\ 9.9\\ 8.8\\ 9.0\\ -21.7\\ 6.0\\ 2255.7\\ 2113.4\\ 14.3\\ 0.6\\ -3.8\\ -2.1\\ -3.3\\ -19.7\\ 5.3\\ v_{dtz^{+}} d\\ \end{array}$	2922.5 -1.0 3.2 11.0 8.1 8.7 -21.3 5.8 2255.5 2116.1 14.3 1.2 -4.5 -2.4 -2.9 -19.4 5.1 v_{dcct}^{d} 2979.5 1475.7 1174.3 175.8 49.1 2235.6 1066.7 908.2 16.4 0	$\begin{array}{c} v_{5} {\rm CH}_{2}, {\rm VEO} \\ \delta_{5} {\rm CH}_{3}, {\rm vBO} \\ \delta_{a5} {\rm CH}_{3}, \delta_{5} {\rm CH}_{3} \\ {\rm \rho CH}_{3}, \delta_{5} {\rm CH}_{3} \\ {\rm \rho CH}_{3} \\ {\rm vCO} \\ \delta {\rm OBO}, \delta {\rm BOC} \\ \delta {\rm OBO}, \delta {\rm BOC} \\ \delta {\rm BOC}, \delta {\rm OBO} \\ {\rm vCD}^{5}, {\rm v}_{5} {\rm CD}_{2}^{2} \\ {\rm v}_{5} {\rm CD}^{3}_{2}, {\rm vCD}^{5} \\ {\rm vBO}, \delta {\rm OBO} \\ \delta_{5} {\rm CD}_{3}, {\rm vCO} \\ \delta_{a5} {\rm CD}_{3} \\ {\rm vCO} \\ {\rm \rho CD}_{3} \\ \delta {\rm OBO}, \delta {\rm BOC} \\ \delta {\rm BOC}, \delta {\rm OBO} \\ \delta {\rm BOC}, \delta {\rm OBO} \\ \delta {\rm BOC}, \delta {\rm OBO} \\ \delta {\rm asCH}_{3} \\ {\rm \rho CH}_{3} \\ {\rm rOBOC} \\ {\rm \tau CH}_{3} \\ \\ {\rm vasCH}_{3} \\ \delta_{a5} {\rm CD}_{3} \\ \delta_{a5} {\rm CD}_{3} \\ \delta_{a5} {\rm CD}_{3} \\ \rho {\rm CD}_{3} \\ \delta_{a5} {\rm CD}_{3} \\ \rho {\rm CD}_{3} \\ \delta_{a5} {\rm CD}_{3} \\ \rho {\rm CD}_{3} \\ \rho {\rm CD}_{5} \\ \end{array}$
d ₉ Species E ⁿ d ₉	V 17 V 18 V 19 V 20 V 21 V 22 V 23 V 15 V 16 V 17 V 18 V 19 V 20 V 21 V 20 V 21 V 20 V 21 V 22 V 23 Mode V 24 V 25 V 26 V 27 V 28 V 27 V 26 V 27 V 27 V 28 V 27 V 29 V 29 V 29 V 29 V 29 V 29 V 29 V 29	1534 1524 1393 1213 1071 530 197 2368 2206 1426 1426 1161 1099 1026 942 500 166 ϖ_{mtz*}^{a} 3166 1515 1200 175 55 2350 1095 927 163 40	$\begin{array}{c} 1512\\ 1498\\ 1369\\ 1194\\ 042\\ 522\\ 173\\ 2311\\ 2166\\ 1406\\ 1135\\ 1081\\ 1004\\ 927\\ 493\\ 153\\ \\ & \varpi_{dtz*}^a\\ \\ \end{array}$	302 1 1519 1502 1378 1200 1047 523 173 2307 2165 1420 1137 1085 1007 930 494 153 00 14 11 18 60 22 10 930 494 153 007 930 494 153 00 14 11 18 60 22 10 91 17 7 43	264 14 1167 30 156 25 9 61 117 1334 192 5 63 17 18 7 7 82 98 84 5 88 84 5 87 83 5 0	10.1 2 21 2 9 6 2 0.8 76 0.6 0.1 1 5 14 3 2 0.6 <i>R</i> _{dtz+} ^b 171 32 8 0.2 0.7 90 12 8 0.4	1494 1485 1363 1200 1042.4 524.7 190 2245 2082 1403 1122.3 1066 1001 919 494 168 vobsd ^c	2898.4 0.8 4.0 0.4 7.5 2.8 -5.6 1.8 2253.7 2099.2 4.1 -3.2 -1.5 0.8 -5.6 1.3 v_{mtz*}^{d} 2979.7 1477.4 1177.4 179.7 65.9 2236.5 1067.0 910.2 166.5 47 3	$\begin{array}{c} 2918.9\\ 0.7\\ 2.6\\ 9.9\\ 8.8\\ 9.0\\ -21.7\\ 6.0\\ 2255.7\\ 2113.4\\ 14.3\\ 0.6\\ -3.8\\ -2.1\\ -3.3\\ -19.7\\ 5.3\\ v_{dtz^{+}} \end{array}$	2922.5 -1.0 3.2 11.0 8.1 8.7 -21.3 5.8 2255.5 2116.1 14.3 1.2 -4.5 -2.4 -2.9 -19.4 5.1 v_{dect}^d 2979.5 1475.7 1174.3 175.8 49.1 2235.6 1066.7 908.2 164.0 35.0	v_{5} CH ₂ , vBO δ_{5} CH ₃ , vBO δ_{5} CH ₃ , δ_{5} CH ₃ ρ CH ₃ ρ CH ₃ ρ CH ₃ ν CO δ OBO, δ BOC δ OBO, δ BOC δ OBO, δ OBO ν CD ⁵ , v_{5} CD ² / ₂ ν_{5} CD ² / ₂ , ν CD ⁵ ν BO, δ OBO δ_{5} CD ₃ , ν CO ρ CD ₃ δ OBO, δ BOC δ BOC, δ OBO Motion v_{a5} CH ₃ ρ CH ₃ τ OBOC τ CH ₃ ν_{a5} CD ₃ ρ CD ₃ τ OBOC τ CD ₅

^a Unscaled harmonic frequency (cm⁻¹) from G03.

 $^{\rm b}\,$ Raman intensity (amu Å $^{-4})$ from G03.

^c Observed frequency (cm⁻¹), where identified. In italics, data used to scale the QC force fields.

^d Calculated scaled frequency (w) or frequency fit (c) form scaled model force field. Calculated vCD values have been premultiplied by 1.011 to compensate for the differing effects of anharmonicity on vCH and vCD stretching frequencies. ^e G03 calculated infrared intensity (km mol⁻¹).

 $^{\rm f}\,$ Corrected for Fermi resonance: see text.

^g From a likely difference band at 869 cm^{-1} (1042 – 869 = 173).

Table 6

"Unsealed" MP2/6-311++G** CH stretching frequencies and infrared intensities in ${}^{11}B(OCHD_{2})_3$ conformers.

Conformer ^a	Point group	ω CH (cm ⁻¹) ^b	$A (\mathrm{km} \mathrm{mol}^{-1})^{\mathrm{c}}$
SSS	C _{3h}	3168.1(a'), 3167.2 (e')	
ssa	<i>C</i> ₁	3167.8, 3167.2, 3138.5	31.5 (H ^a)
sa1a1	<i>C</i> ₁	3167.5, 3138.5, 3138.4	38.5 (H ^s)
sa ₁ a ₂	<i>C</i> ₁	3167.5, 3138.6, 3138.3	38.5 (H ^s)
a ₁ a ₁ a ₁	C3	3138.6(a), 3138.4(e)	
ala1a2	<i>C</i> ₁	3138.7, 3138.4, 3138.3	

^a Hydrogen atoms "H^s" are in the skeletal plane; "H^{ai}", "H^{a2}" are above and below this plane respectively. Differences in ω CH for a given type of bond in any one conformer are indicative of the small degree of coupling between the motions of the two like C-H bonds concerned.

^b Double degeneracy is found only with the sss and $a_1a_1a_1$ conformers. In italics, the frequency for which the IR intensity is given in column four.

 $^{\rm c}\,$ Infrared intensity for the stretching of the unique C–H $^{\rm a}$ or C–H $^{\rm s}$ bond present in this conformer.

tions for dimethylether (DME), for whose v^{is} CH bands both frequency and IR intensity data are available from experiment. [15]. The DME results, seen in Table 7, show that a fair agreement is obtained between theory and experiment, bearing in mind the small differences expected between harmonic and anharmonic data. (The fall in $\Delta \omega_{is}$ CH from about 108 cm⁻¹ (mtz+) in DME to 29.5 cm⁻¹ in TMB gives an indication of the extent to which the π electrons on the oxygen atoms in TMB have been delocalized.) This confirmation of the reliability of QC estimates points to a conflict between the QC and the earlier v^{is} CH evidence which will be discussed further in detail below.

Among other types of motion, consistent features of all the QC predictions of vibration frequency are the low methyl torsional frequencies, which lie in the range 40–61 cm⁻¹ for the d_0 species (see Table 5). This feature makes it very likely that at room temperatures there will be significant populations of molecules in excited torsional states, including those above the barrier to methyl torsion. To this state of affairs we attribute some of the breadth and lack of characteristic structure observed in most of the gas phase band contours.

5. Results: Assignments of observed spectra and force field scale factors

The 28 normal modes of the molecule, together with their spectral activity, infrared (IR) or Raman (R), are distributed as follows: 8 A' (R,pol.); 6 A" (IR); 9 E' (IR, R,dp); 5 E" (R,dp). The A" infrared bands should in the gas phase exhibit the contour of a parallel band of an oblate symmetric top, with a prominent narrow central Q branch. However, the gas phase contours of the E' infrared bands are expected to be variable in nature. No attempt was made to interpret gas phase Raman band contours.

Table 7

Computed harmonic frequency ω and infrared intensity A for C–H stretching bands in (CHD_2)(CD_3)O.

Parameter	dtz+	dcct	mtz+	mcct	Obsd. ^a
$\omega \text{CH}^{\text{s}}(\text{cm}^{-1})$	3106.3	3100.0	3174.0	3170.8	2985
$\omega CH^{a} (cm^{-1})$	2990.3	2986.7	3066.0	3064.2	2883
$\Delta \omega_{s-a} (cm^{-1})$	116.0	113.3	108.0	106.6	102
ACH ^s (km mol ⁻¹)	29.3	30.3	25.9	24.4	25.8 ^b
ACH ^a (km mol ⁻¹)	67.8	64.9	57.1	51.8	47.5 ^b
ΔA_{a-s} (km mol ⁻¹)	38.5	34.6	31.2	27.4	21.7 ^b

 a Observed anharmonic frequency and IR intensity data for the species $(CHD_{2})_{2}O$ from reference [15].

 $^{\rm b}$ Partial overlap between the two $\nu^{\rm is}CH$ bands leads to some uncertainty in the division of intensity between each.

As well as the assistance from the calculated IR and R intensities in Table 5, substantial help in assigning bands was derived from our measured isotopic frequency shifts. Values for the ${}^{12}C{-}^{13}C$, ${}^{11}B{-}^{10}B$ and ${}^{11}B{}^{12}C{-}^{10}B{}^{13}C$ frequency shifts calculated from the scaled mtz+ force field are listed together with observed ${}^{12}C{-}^{13}C$ shifts in Table 8.

5.1. vCH and vCD regions

Analysis of these regions in a methyl-containing compound is normally difficult due to the universal Fermi resonances (FRs) occurring between the fundamental levels and those of overtones and combinations of methyl deformations. These resonances are particularly marked in Me–O compounds due to the high frequencies of the $\delta_{as}Me$ and δ_sMe modes in such molecules [16]. An additional complicating factor in TMB is the mixing of $v_{as}BO_3$ motion into the E' modes in the 1450–1500 cm⁻¹ region of d_0 . This could lead to differing effects of FR on the A' and E' fundamental bands in the vCH region. Apart from this possible effect, the lack of coupling between CH stretching motions in different methyl groups

Table 8

Isotope frequency shifts $\Delta\nu~(cm^{-1})$ from the $^{11}B(O^{12}CH_3)_3$ species to the tsotopomers $^{11}B(O^{13}CH_3)_3$, $^{10}B(O^{12}CH_3)_3$ and $^{10}B(O^{13}CH_3)_3$, as calculated from the scaled mtz+force field.

A'					
Mode		$-\Delta v (^{13}C$:)		Motion
		calc	C	obsd	
<i>v</i> ₁		11.2	-	-	vCH ^s
<i>v</i> ₂		2.7	-	-	$v_{s}CH^{a}_{2}$
<i>v</i> ₃		2.2	1	(5)	$\delta_{as}CH_3$
v_4		5.5	5	5(1)	$\delta_{s}CH_{3}$
v ₅		10.0	-	-	ρ CH3, vCO
v ₆		13.9	2	20(3)	vCO, ρ CH ₃
v ₇		6.0	-	-	vBO, vCO
v ₈		5.8	6	5(1)	δBOC
A″					
Mode	$-\Delta v(^{13}$	C)	$\Delta v(^{10}\text{B})$	$\Delta v(^{10}\mathrm{B}^{13}\mathrm{C})$	Motion
	calc	obsd	calc	calc	
v ₉	11.2	10.8(7)	0.0	-11.2	$v_{as}CH_2^a$
v ₁₀	1.9	_	0.0	-1.9	$\delta_{as}CH_3$
<i>v</i> ₁₁	8.3	_	0.0	-8.3	$\rho'' CH_3$
v ₁₂	0.0	FR	26.6	26.6	$\delta_{\perp} BO_3$
V13	1.2	1.6(2)	0.4	-0.8	τ OBOC, τ CH ₃
v_{14}	0.1	-	0.0	-0.1	τCH_3 , $\tau OBOC$
E'					
Mode	$-\Delta v(^{13}$	C)	$\Delta v(^{10}\text{B})$	$\Delta v(^{10}B^{13}C)$	Motion
	calc	obsd	calc	calc	
v ₁₅	11.2	FR	0.0	-11.2	vCH ^s , v _s CH ^a
v ₁₆	2.6	FR	0.0	-2.6	$v_{s}CH_{2}^{a}$, vCH^{s}
V ₁₇	2.7	3.3(4)	16.0	13.9	$\delta_{s}CH_{3}$. vBO
v ₁₈	2.5	2.5(4)	0.4	-1.7	$\delta_{as}CH_3, \delta_sCH_3$
v ₁₉	4.1	6(1)	29.2	24.5	vBO, $\delta_s CH_3$
V20	8.9	10(2)	2.1	-7.0	ρ' CH3
v ₂₁	16.8	18.0(7)	4.2	-12.9	vCO
V22	4.3	5(1)	1.6	-2.6	δ OBO, δ BOC
V ₂₃	4.3	3(3)	0.3	-4.0	$\delta BOC, \delta OBO$
Ε"					
Mode			$-\Delta v(^{13}C)$		Motion
			calc		
v ₂₄			11.1		$v_{as}CH_2^a$
V ₂₅			2.0		$\delta_{as}CH_3$
v ₂₆			8.3		$\rho'' CH_3$
V ₂₇			0.8		τΟΒΟϹ
			0.1		τCH_{2}

mentioned above means that interpretation of frequencies may be carried out as for a single methyl group.

In the past, successful interpretations of the vCH regions of MeO containing molecules have depended on experimental data for CHD₂-substituted compounds which yield v^{is} CH values [17]. The effect of the two lone pairs on the oxygen atom is to lower v^{is} CH^a relative to v^{is} CH^s. The degeneracy of the E vibrations of a methyl group of C_{3v} local symmetry is thereby lifted, resulting in the frequency sequence v_{as} CH₃(a') > v_{as} CH₃(a'') > v_{s} CH₃(a') [17]. Here the subscripts "s" and "as" have lost some of their original significance. Delocalisation of the oxygen lone pairs to the boron atom will of course lessen this effective loss of symmetry by reducing the difference in C–H bond strength.

In the case of TMB, the IR spectrum of $B(OCHD_2)_3$ (hereafter, d_6) is complex [4]. The main, low frequency band has a sharp low frequency cut-off leading to a O branch at 2950.4 cm⁻¹. This is followed by two more O branches at 2953 and 2956 cm⁻¹ which merge into broad absorption on which there is a prominent shoulder at 3012 cm⁻¹. A plausible interpretation of this spectrum is that the lowest Q branch comes from transitions involving stretching of the CH^a bond in the ground torsional state of the molecule while the higher Q branches derive from progressively higher excited torsional states. In the latter the mean orientation of the C-H^a bond should progressively approach closer to the skeletal plane, thereby increasing its strength. This interpretation is to be preferred to the alternative one in which the three Q branches are ascribed to different d₆ conformers, since the QC evidence, as seen in Table 6, indicates that these should yield identical vCH^a frequencies, rather than ones differing by $2-3 \text{ cm}^{-1}$.

With the previous ascription of the shoulder in the d₆ spectrum at $3012 \text{ cm}^{-1} \nu^{is}\text{CH}^{s}$, the resulting difference in $\nu^{is}\text{CH}$ becomes $3012 - 2950.4 = 61.6 \text{ cm}^{-1}$.

Alternative evidence for the difference in C–H bond strength has come from the local mode study of Mananzares et al. [5]. In their gas phase spectra these authors identified two individual broad bands as arising from $\Delta v = 5$ and 6 transitions respectively. These broad bands by deconvolution each yielded two peaks, which when fitted to a Birge–Sponer quadratic expression yielded values of ω_e of 3089 and 3051 cm⁻¹. While thus result must be considered as preliminary, it may be significant that the difference of 38 cm⁻¹ between the two ω values is larger than the ~29 cm⁻¹ predicted by the QC studies, though much less than the 61.6 cm⁻¹ derived from the CHD₂ study [4].

In attempting to use QC evidence in analysing the vCH region several kinds of difficulty are encountered. In large measure these stem from the circumstance that we will be attempting to interpret observed, *anharmonic* frequency data by the use of QC based *harmonic* force fields. The latter will therefore require scaling if observed frequency data are to be fitted. The first difficulty arises from the evidence that QC models at the level of theory we are able to employ in this study may not reproduce quantitatively the difference in CH bond strength to be encountered. Several instances of this are known [18,19]. Differing scale factors therefore may well be needed for the stretching of each of the two kinds of C–H bond present in TMB. This explains the reason for our choice of CH stretching symmetry coordinates, described above.

A second difficulty arises from recent findings which suggest that CH stretching anharmonicity can vary according to the type of vibration involved, for instance, whether the stretching is symmetric or antisymmetric in nature [20,21]. A scale factor based on v^{is} CH frequency data may then not be strictly applicable to the stretching motions of a CH₃ group. Variation in anharmonicity may also occur from one v^{is} CH motion to another. However, exploration of the effect of anharmonicity variation is beyond the scope of the present study.

A third difficulty is the possibility of error in the QC calculations of the interaction force constants which couple the motions of individual C–H bonds to produce the stretching vibrations in a CH_2 or CH_3 system. Such interaction force constants are typically smaller from MP2 model calculations than they from DFT based ones. [20–24] Evidence suggests that the MP2 constants are to be preferred to DFT ones [20,21]. For this reason we will confine our discussion of the vCH region to results from the mtz+ model.

Faced with the varying estimates given above of the relative strengths (in cm⁻¹) of the two kinds of CH bond, it is natural to ask if there is alternative evidence bearing on vCH scale factors to be found in the spectra of the normal (d_0) or fully deuterated (d_9) species. The only such datum to be found, which might be useful in determining a vCH scale factor, is the frequency of $v_9(a'')$. The parallel-type band due to this mode is readily identified by means of the narrow Q branch seen at 2980.2 cm⁻¹ in d₀ and at 2235 cm⁻¹ in d₉. The d₀ band exhibits a 13 C shift of 10.8 cm⁻¹ in good agreement with that predicted for this mode from our QC models. Evidence from other methyl-containing molecules points to FR effects on asymmetric stretching vibration band frequencies s to be much smaller or even negligible compared with those operating on v_{s} CH₃ levels [17]. v_{9} , otherwise represented as v^{as} CH₂^a, involves motions of the CH^a bonds only and the frequency of v_9 therefore provides directly a scale factor for the stretching of the latter bond.

In Table 9 we explore four different ways of scaling the stretching force constants of the two kinds of CH bond and the effect these have on the prediction of all the CH and CD frequencies in the d_0 , d_9 and d_6 species. The data used to define scale factors are given in bold.

First, a word of caution is needed. In attempting to account for both vCH and vCD frequencies with a single set of scaled force constants, we need to remove as far as possible the effects of the differing anharmonicities affecting vCH and vCD vibrational transitions. This we have done in Table 9 by the usual expedient

Table 9

Variations in vCH and vCD frequencies (cm^{-1}) with scale factor (sf) from the mtz+ model force field.

Parameter	(a) ^a	(b) ^a	(c) ^a	(d)	$v_{obsd}(IR_{gas})$	$v_{obsd}(R_{gas})$
sfCH ^s	(0.8858) ^b	0.9039	0.9039	0.8898		
sfCH ^a	0.8858	0.8858	0.8837	0.8837		
v ^{is} CH ^s	2981.7	3012.0	3012.0	2988.4 ^c	3012.0?	
v ^{is} CH ^a	2953.9	2953.9	2950.4	2950.4	2950.4?	
A' d ₀ v_1	3001.8	3026.8	3026.3	3006.4	?	2999
<i>v</i> ₂	2899.4	2904.4	2901.4	2897.7	FR	FR
A' d ₉ v ₁	2253.5	2270.7	2270.1	2256.5	2245	2245
V2	2100.2	2105.4	2103.4	2099.6	2105 ^{°d}	2106 ^{°d}
A" d ₀ v ₉	2980.2	2980.2	2976.7	2976.7	2980.2	
A" d ₉ v ₉	2236.8	2236.8	2234.1	2234.2	2235	
E' d ₀ v ₁₅	3001.7	3026.6	3026.0	3006.2	?	2999
v ₁₆	2898.4	2903.9	2900.9	2897.1	FR	FR
E' d ₉ v ₁₅	2253.7	2270.7	2270.1	2256.7	2245	2245
V16	2099.2	2104.5	2102.6	2098.6	2105 ^{°d}	2106 ^{°d}
E" d ₀ v ₂₄	2979.7	2979.7	2976.1	2976.2		?
E″ d ₉ v ₂₄	2236.5	2236.5	2233.9	2233.9		?
$(v_{15}-v_9)^{e}$	21.5	46.4	49.3	29.5	19?	
do						
$(v_{15}-v_9)^{e}$	16.9	33.9	36.0	22.5	10?	
d ₉						

^a In bold, data used to fix the two vCH scale factors, All calculated vCD values have been premultiplied by 1.011.

^b Constrained to value for sfCH^a.

^c v^{is} CH^a + $\Delta \omega$. where $\Delta \omega = \omega^{s} - \omega^{a} = 48 \text{ cm}^{-1}$ from the local mode study of Manzanares et al. [5].

Deperturbed value from a rough estimate of FR.

^e These differences give a close measure of the splitting of the $v_{as}CH_3$ modes into A' and A" components in an individual methyl group. An alternative measure of this splitting, $v_{15}-v_{24}$, is about 0.5 cm⁻¹ larger.

of multiplying by 1.011 all vCD frequencies calculated from force constants fitting observed vCH data [17].

Under (a) we use the $d_0 v_9$ frequency to define the scale factor for the stretching of the CH^a bond and assume this same factor to apply to CH^s bond stretching. The close prediction (2236.8 cm⁻¹) of the v_9 band observed at 2235 cm⁻¹ in d_9 , is pleasing as it suggests that the effects of FR on v_9 are small, bearing in mind the approximation involved in the 1.011 factor. v^{is} CH^a is predicted at 2953.9 cm⁻¹ which is within 3.5 cm⁻¹ of the value of 2950.4 assigned from the d_6 spectrum. The small difference between these two estimates for v^{is} CH^a could easily derive from a small residual FR on v_9 or from a difference in the intrinsic anharmonicities of the v^{is} CH^a and v^{is} CH^a motions. There is therefore no case at present for reinterpreting this part of the d_6 spectrum, at least. However, the value predicted for v^{is} CH^s, 2981.7 cm⁻¹, is considerably less than the 3012 cm⁻¹assigned in [4].

Under (b) we use two scale factors, one for $v^{is}CH^s$ based on the 3012 cm⁻¹ shoulder, the other, for $v^{is}CH^a$ based on v_9 . A substantial difference of 0.018 appears in the resulting scale factors and the values of v_1 (A') and v_{15} (E') now differ significantly from their predicted values under (a).

In the refinement under (c) we use the two d_6 based v^{is} CH values, with very little change from the predictions made under (b).

Under (d) we utilise the local mode data by taking their $\Delta \omega^{is}$ CH difference of 38 cm⁻¹ to approximate a similar Δv^{is} CH value and adding the latter to our v^{is} CH^a of 2950.4 cm⁻¹, to give v^{is} -CH^s = 2988.4 cm⁻¹, The resulting predictions of v_1 , v_{15} etc. are then fairly close to those under (a).

Comparing the results from (a)–(d), we see only a modest variation of up to 7 cm⁻¹ in the predictions of v_2 , but somewhat larger variations of up to 25 cm⁻¹ in v_1 in d₀ and d₉.

In comparing these predictions with experimental data, it is evident that little can be deduced from the observed values of v_2 , which are strongly affected by FR. This is particularly evident in the Raman spectrum of d₀ where there are no less than seven polarised lines between 2978 and 2728 cm⁻¹ showing the small ¹³C shifts expected from v_2 , v_{16} and associated overtone and combination levels. Suggestions for the latter are included in Table 1. However, in d₉ there are only two polarised lines, at 2146 (IR: 2145) and 2087 (IR 2086) cm⁻¹. If the former is the overtone of 1067 cm⁻¹, its deperturbed position might be estimated to lie near $2 \times 1067 - 7 = 2127 \text{ cm}^{-1}$, yielding a FR shift of about 19 cm⁻¹ and placing v_2^* near 2106 cm⁻¹. Remembering that this estimate includes both FR and normal anharmonicity corrections, we can only claim that all four estimates of the position of v_2^* (d₉) are in the right range.

A more severe problem arises in attempting to assign v_1 (a') and v_{15} (e'), which are expected to coincide. The splitting between either of these modes and v_9 (a"), shown at the bottom of Table 9, represents the splitting mentioned above of the degenerate $v_{as}CH_3$ modes of a methyl group of $C_{3\nu}$ local symmetry, due to insertion of the BO₃ plane.

In the spectra of d₉ there is only one feature capable of assignment to either or both of v_1 and v_{15} , and that is the band at 2245 cm⁻¹, seen in both the IR and Raman spectra. The splitting from v_9 at 2135 cm⁻¹ is then only 10 cm⁻¹, rather less than the smallest separation shown in Table 9, that of ~17 cm⁻¹ under option (a).

A similar situation is found in the spectra of d_0 . Here a definite band with large appropriate ¹³C shift is seen in the Raman spectrum at 2999 cm⁻¹. Intensities calculated from the dtz+ model, Table 5, suggest that this band represents v_{15} more strongly than v_1 . The splitting between this frequency and that of v_9 at 2980.2 cm⁻¹ is then only 19 cm⁻¹. However, this is now compatible with the splitting of 21.5 cm⁻¹ predicted under (a), when the likely effects of small resonances and experimental error are borne in mind. We were unable to assign v_{15} in the IR spectrum of d_0 due to the diffuseness of the band contour in this region, but it can be discerned at 2992 cm⁻¹ in CCl₄ solution [3] and in the solid at 2999 [7].

If these analyses of the d_0 and d_9 spectra are correct, then $v^{is}CH^s$ cannot be as large as 3012 cm⁻¹ as originally assigned [4]. We may also expect that a more extended study of local mode spectra will revise the value of $\Delta \omega$ downwards.

5.2. Assignments: other fundamentals

A' class. Apart from the vCH and vCD vibrations, discussed above, modes which give rise to difficulty in assignment are v_3 and v_5 in d₀ and v_4 in d₉. v_3 (d₀) will certainly contribute to the broad δ CH₃ band at 1470 cm⁻¹. v_5 has previously been assigned to a weak Raman band in the solid state, either at 1183 cm⁻¹ [3] or at 1208 cm⁻¹ [7]. Our scaled force field predicts this mode at about 1217 cm⁻¹ in the gas, in fair agreement with the later estimate. In d₉, a weak, sharp shoulder in the Raman spectrum at 1087 cm⁻¹, possibly polarised, is a likely candidate for v_4 , predicted at 1083 cm⁻¹. v_5 is presumed to contribute to the 1067 cm⁻¹ band along with other δ CD₃ modes.

A'' class. The assignments in d₀ of v_{12} (667.4 cm⁻¹ and v_{13} (102.8 cm⁻¹) are non-controversial and follow the earlier studies [3,7]. However, as commented on earlier [4], there is clear evidence for a Fermi resonance on v_{12} , the out-of-plane BO₃ bending mode, from the IR spectra of both d₀ and d₉ isotopomers, illustrated in Fig. 2.

The ${}^{10}B-{}^{11}B$ frequency shift calculated for this mode is close to 27 cm⁻¹ (Table 8) in both d₀ and d₉ species, while the d₀ to d₉ shift should be 2–3 cm⁻¹(Table 5). By contrast the ${}^{12}C-{}^{13}C$ shift is predicted to be zero.

The IR Q branches at 702.0 and 678.0 cm⁻¹ in d₉ are undoubtedly the ¹⁰B and ¹¹B components of v_{12} , but their separation of 24 cm⁻¹ is 3 cm⁻¹ less than expected, while the expected deuteration shift on the ¹¹B band is absent. However, an additional, broader weak band appears at about 648 cm⁻¹.

In the d_0 spectrum where a single ¹⁰B band due to v_{12} would be expected, two bands appear at 711.4 and 699.8 cm⁻¹ which yield separations of 44.0 and 32.4 cm⁻¹ from the ¹¹B v_{12} frequency of 667.4 cm⁻¹. Moreover, both these higher bands carry significant $^{12}C^{-13}C$ frequency shifts, ~3 and ~5 cm⁻¹ respectively. A smaller such shift can also be discerned in the 677.4 cm⁻¹ band. All these features are explained by a FR involving the combination level $v_{22}(e') + v_{27}(e'')$ which is predicted to lie above $v_{12}(^{11}B)$ in d₀ but below v_{12} (¹¹B) in d₉. An exact reproduction of the observed frequencies is not possible but rough calculations with an interaction parameter $W_{12,23,27}$ of about 13 cm⁻¹ suggest that the FR shift on v_{12} (¹¹B) has been about 6 cm⁻¹ downwards, placing the deperturbed v_{12}^* at about 673 cm⁻¹. By contrast, v_{12} in d₉ has been displaced upwards, by about 7 cm⁻¹ (¹¹B) or ~ 4 cm⁻¹ (¹⁰B), yielding values for the deperturbed v_{12}^* of ~671 cm⁻¹. (¹¹B) or 698 cm⁻¹ (^{10}B) . The 699.8 (d_0) and 648 cm⁻¹ (d_9) bands are each assigned as $v_{22} + v_{27}$ in he ¹¹B species, which on the basis of a zero value of $x_{22,27}$ yields values of v_{27} of $700 - 6 - 525 = 169 \text{ cm}^{-1}$ in d₀, and $648 + 7 - 494 = 161 \text{ cm}^{-1}$ in d₉. (There is no boron isotope shift in the E" species.) The additional ¹⁰B band at 711.4 cm⁻¹ is assigned to a more strongly perturbed $v_{22} + v_{27}$ level, perhaps a 50/50 mixture, with the other ¹⁰B component level lying at about 691 cm⁻¹ and so far unidentified in the complex absorption in this region.

For the assignment of v_{11} , a Q branch is seen at 908.7 cm⁻¹ in d₉, but there is no corresponding gas phase feature in d₀ at the expected value of ~1175 cm⁻¹. The infrared intensity predicted for the latter is very low, which provides a likely explanation for its non-observance in the gas. However, v_{11} has previously been assigned to a solid state shoulder at 1184 cm⁻¹.[7] v_{10} (δ_{as} CH₃) in



Fig. 2. Infrared spectra of TMB species in the region of v_{12} , showing Fermi resonating bands.

d₀ could not be distinguished in the complex absorption in the 1450–1520 cm⁻¹ region and its δ_{as} CD₃ counterpart is likely in the same way to be part of the 1066 cm⁻¹ IR band in d₉. Refining to the latter value then predicts v_{10} in d₀ near 1477 cm⁻¹. Neglect of d₀/d₉ anharmonicity differences means that the d₀ value is likely to be lower still. The earlier assignment of v_{10} to 1509 cm⁻¹ [7] therefore seems unlikely.

Finally, a plausible value of 49 cm⁻¹ is obtained for v_{14} from the very weak IR band at 780 cm⁻¹ if this is interpreted as the combination 731 (v_7 , A') + 49 (v_{14} , A'') = 780 cm⁻¹, (A''). Torsional frequencies are also expected to combine with antisymmetric CH₃ stretching modes to give weak shoulders above v_{as} CH₃ bands [25] and such shoulders can in fact be seen (see Table 1).

E' class. The assignment of v_{17} in d₀, which in this isotopomer is a coupled vBO/δ_sCH_3 motion, to the IR bands at 1509 (¹⁰B) and 1494 cm⁻¹ (¹¹B) is strongly supported by its observation at 1448.7 (¹⁰B) and 1403.5 cm⁻¹ (¹¹B) in d₉. The force constant refinement results show how this large vB–O isotope shift of 45 cm⁻¹ in d₉ is in d₀ split between v_{17} and v_{19} , the latter seen at 1363 cm⁻¹ (¹¹B).

Elsewhere there are problems associated with assignment of the methyl rocking frequency v_{20} in d_0 and with the skeletal bend

 v_{23} in both d_0 and d_9 . In the gas phase infrared spectrum of d_0 the ¹³C shift of about 10 cm⁻¹ on the band at 1200 cm⁻¹ is compatible with an assignment to v_{20} , as in [7], but is incompatible with the earlier choice of the combination $v_{21} + v_{28}$ (A") [3], for which the ¹³C shift should be ~18 cm⁻¹. However, the corresponding gas phase Raman band is broad and rather lower in frequency. This may be in part because it arises from both v_{20} (e') and v_{27} (e"), the latter predicted 13–16 cm⁻¹ below the former (Table 5). In the Raman liquid spectrum of Stampf et al. [7] two depolarised lines are resolved at 1171 and 1165 cm⁻¹ which fit quite well the expected positions of these two fundamentals if there are significant gas/liquid shifts. However, a value for the centre of v_{20} (d_0) in the gas near 1193 cm⁻¹ would be more commensurate with the corresponding value of 1001 cm⁻¹ in d_9 .

A somewhat similar situation arises near 190 cm⁻¹ where the infrared gas phase band due to v_{23} (d₀) is observed at 190 cm⁻¹, slightly above the Raman band at 184 cm⁻¹ which can arise from both v_{23} (e') and v_{27} (e''), predicted to have similar intensities. However, the ¹³C shift of about 4 cm⁻¹ on this Raman band is consistent only with its assignment to v_{23} (e'). The d₉ infrared band at 168 cm⁻¹ fits well with the position expected for v_{23} .

E" class. The only d₀ fundamental for whose position there is significant evidence is v_{27} . The analysis outlined above of the FR affecting v_{12} placed v_{27} near 169 cm⁻¹. With v_{14} at 103 cm⁻¹, $v_{14} + v_{27}$ (E') is predicted to be 272 cm⁻¹, providing an explanation for the weak IR feature at 273 cm⁻¹. The weak, polarised Raman line at 331 cm⁻¹ may at the same time be assigned as the first overtone of v_{27} . A slightly higher value for v_{27} of 173 cm⁻¹ is obtained from the infrared band at 869 cm⁻¹ if the latter is the difference $v_{21} - v_{27}$ (1042 – 173 = 869 cm⁻¹), as the large 18 cm⁻¹ ¹³C shift suggests. Transfer of the appropriate mtz+ scale factors from the A" class predicts v_{27} to be 180 cm⁻¹.

The scaled mtz+ value of 1177 cm^{-1} for v_{26} (d₀) may be compatible with one of the two liquid phase Raman lines 1171, 1165 cm^{-1} , observed by Stampf et al. [7], if there is a significant downwards shift upon condensation. In a similar manner, the predicted value for v_{28} of 64 cm^{-1} is compatible with the assignment of this mode to the solid phase Raman frequency of 78 cm^{-1} [7], since the upwards shift here of 14 cm^{-1} is acceptable for the effect of condensation on a methyl torsion.

Locating v_{24} and v_{25} , predicted at 2980 and 1477 cm⁻¹, does not appear to be currently feasible.

In d₉, v_{26} is seen as a Raman line at 908 cm⁻¹ in the liquid, close to its predicted value of 910 cm⁻¹.

5.3. Overtone and combination bands

Some of the earlier assignments of Rogstad et al. for d_0 are confirmed by the ¹³C shifts shown in Table 1 but not all. However, the error in the measured shifts may be greater than those indicated in this table, due to the breadth of the peaks measured. In particular the shifts observed on the seven polarised Raman lines involved in the v_2 FR system, whose origin can hardly be doubted, are generally less than anticipated.

The large ¹³C shift of 29 cm⁻¹ on the band at 2400 cm⁻¹ can only be accounted for by the ternary combination $v_{11} + v_{21} + v_{23}$ (A"). The simpler alternatives of $2v_{20}$ or $v_{19} + v_{21}$ involve ¹³C shifts of only 18 or 21 cm⁻¹.

In the spectrum of d_9 , the absence of ¹³C shift data made it impractical to list in Table 2 the many combination and overtone permutations possible.

A final comment regarding the interpretation of the IR spectra is that the problems presented by the breadth and diffuseness of the bands would be greatly eased if spectra were to be obtained in liquefied noble gas solution. [26] Such a study is greatly to be desired.

5.4. Force fields, scale factors and frequency fits

The scale factors for the three model force fields are shown in Table 10, grouped according to the type of motion involved. With the objective of testing each model force field for self consistency, we set out to determine as many individual scale factors as possible. This might permit testing of the common practice of assuming identical scale factors for a particular type of internal coordinate, for example, all those involved in CH bending motions. In the event, the complexity of bands in the 1400–1500 cm⁻¹ (d₀) and 1000–1100 cm⁻¹ (d₉) regions made this difficult. We were therefore obliged to constrain certain scale factors equal, for instance, in the case of the δ_s CH₃ and δ'_{as} CH₃ pairs in the A' and E' species. The same problem as it affected the vCH^s and vCH^a stretching force constants has been discussed in detail above, see Table 9. Of the options in Table 9 we selected for use in Table 10, that under (a) which employs a single vCH scale factor based on the value of v_9 in d₀.

The frequency fits given by the three model force fields are included in Table 5, while the preferred mtz+ scaled force field is given in the Supplementary Data, Table 2.

Two major anomalies can be seen in the frequency fit data. The first is associated with the predictions of v_2 and v_{16} which are up to 20 cm⁻¹ higher from the B3LYP models than they are from the MP2 model. This difference can only derive from a difference in calculated CH stretch/CH stretch interaction force constants, as found previously in a number of instances [20–24]. If the rough FR correction applied above to v_2 is correct, comparison with the v_2 and v_{15} frequencies predicted in Table 5 strongly favours the MP2 result.

A more striking example of the superiority of the mtz+ force field is seen in the failure of the B3LYP models to fit the E' modes v_{22} and v_{23} . These vibrations are composed of strongly coupled δ OBO and δ BOC motions and the failure of the two DFT models to reproduce their frequencies, especially in the d₉ isotopomer, is readily traced to the lower DFT values of the interaction force constant $F_{16,18}$ linking the two motions: $F_{16,18} = 0.1008$ (mtz+), 0.0720 (dtz+), 0.0716 (dcct) aJ rad⁻².

It is also of interest to compare the scale factors (sf) from the three models.

Within the uncertainties, often substantial, of the sf values for the various methyl motions, there is little to indicate variation in the $\delta_{as}CH_3$, δ_sCH_3 or ρCH_3 factors with choice of origin. A possible exception to this is the in-plane methyl rocking factor from the

Table 10

Scale factors for symmetrised QC force fields for trimethoxyborane.

Motion type	Symmetry coordinate ^a				Scale factor		
	A′	Α″	E′	E″	mtz+	dtz+	dcct
vCH _s , vCH _a	4, 5	12	19, 20	26	0.886 ^b	0.931 ^b	0.934 ^b
$\delta_{s}CH_{3}, \delta'_{as}CH_{3}$	6, 7				0.936(3)	0.964(4)	0.959(3)
$\delta_{s}CH_{3}$,			21,		0.942(5)	0.978(18)	0.973(18)
$\delta'_{as}CH_3$			22				
$\delta_{as}'' CH_3$		13		27	0.950(39)	0.975(9)	0.969(9)
$\rho' CH_3$	8				0.938(9)	0.978(8)	0.975(8)
$\rho' CH_3$			23		0.968(8)	0.993(28)	0.984(27)
$\rho'' CH_3$		14		28	0.965(40)	0.997(9)	0.984(9)
τCH_3		11		25	1.004(60)	0.945(6)	0.963(7)
$v_{s}BO_{3}$	1				0.941(8)	0.991(9)	0.989(8)
$v_{as}BO_3$			15		0.957(9)	0.956(30)	0.934(29)
vCO	2				0.965(10)	0.992(10)	0.976(10)
vCO			17		0.934(9)	0.970(30)	0.963((30)
$\delta_{ }BO_3$			16		1.016(6)	1.138((21)	1.134(21)
$\delta_{\perp}BO_3$		9			0.961'(29)	0.980(6)	1.001(7)
$\delta_{ }BOC$	3		18		1.011(5)	1.105(5)	1.104(5)
τΟΒΟϹ		10		24	1.476(192)	0.925(17)	0.646(12)

^a In italics, location of constrained scale factors.

^b Refined to give exact fit to v_9 (A) = 2980.2 cm⁻¹ in TMB-d₀.

mtz+ model which is significantly larger from the E' species than it is from the A'. The mtz+ model also requires a τ CH₃ factor larger than that for any of the other methyl motions.

Among the skeletal motions, the mtz+ model yields a better agreement between the factors for symmetric and antisymmetric BO stretches than do the dtz+ or dcct models, although the error in the $v_{as}BO_3$ factor is large for the latter. This is associated with a smaller vBO/vBO constant, f (unscaled mtz+value of 0.6185 aJ Å⁻²) than is found with the B3LYP models (f = 0.6646 (dtz+), f = 0.6714 (dcct). This repeats the pattern found for the stretching of C–F and C–Cl bonds n 1,1-difluorocyclopropane [20] and dichloromethane [21]. Stretch/stretch interaction force constants f are smaller and the v_{as} and v_s scale factors closer together from MP2 models than they are from B3LYP ones. This has been considered to be an advantage of the former [20,21].

Another difference between the MP2 and DFT models is seen with the $\delta_{||}BO_3$ and $\delta_{||}BOC$ factors which are significantly larger than average for the DFT ones.

Perhaps the most curious set of scale factors is that associated with the τ OBOC coordinate, S_{10} . These vary from very large (1.48) for the mtz+ model to very small (0.646) for the dcct one. By contrast the dtz+ value of 0.925 is almost average in value. A similar large variation in scale factor was discovered in butadiene, associated with the out-of-plane bending modes [27]. However, in the latter case, the source of the anomalous scale factors could be attributed to the absence of f functions in the 6311++G** basis set [27] and the anomalies disappeared when the cc-pVTZ basis, which employs such f functions, was used. Clearly a similar explanation cannot apply to the τ OBOC factor in TMB. The marked variability in this last scale factor points to a general need for caution in utilising QC calculations for the estimation of out-of-plane bending motions of planar systems, particularly when these derive from extended atomic arrays where long range interactions between non-bonded atoms may be important.

The full set of symmetry force constants from the scaled mtz+ model is available in the Supplementary Data, Table S2.

6. Conclusions

- 1. New vibrational spectra of labelled trimethoxyborane species, aided by scaled QC-based force fields, enable a more reliable set of fundamental frequencies to be established for B(OCH₃)₃ and a new such set for B(OCD₃)₃.
- 2. The change in stability with basis set from cis- to $trans-C_{3h}$ structure is demonstrated using HF, B3LYP and MP2 models.
- 3. A combined use of the QC results and IR spectra in the CH and CD stretching regions indicates that the difference in C–H bond strength between the two kinds of CH bond present is much less than had been previously diagnosed from a B(OCHD₂)₃ spectrum, indicating the need for a reinterpretation of the latter. This conclusion is supported by similar data for dimethylether.
- 4. A Fermi resonance involving v_{12} (a") is identified and treated approximately.
- 5. Evidence is found for the superiority of MP2-based force fields over those from B3LYP models.
- 6. Anomalous scale factors are found associated with the τ OBOC torsional motion.

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Appendix A. Supplementary data

Symmetry coordinates for trimethoxyborane, Table S1; scaled MP2/6-311++G** symmetry force constants, Table S2; infrared survey spectrum, 400 to 2400 cm⁻¹, of $B(OCD_3)_3$, Figure S1. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2010.02.073.

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