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Ha Vinh Lam Nguyen, Maike Andresen, Wolfgang Stahl

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Ha Vinh Lam Nguyen†[a,b], Maike Andresen[a,c] and Wolfgang Stahl[c]††

The microwave spectrum of the fruit ester methyl valerate was recorded using two molecular jet Fourier transform spectrometers covering the frequency range from 2 to 40 GHz. Quantum chemical calculations yielded 11 minima for the *anti* ester configuration, among them two were identified in the experimental spectrum. The methyl group in the methoxy moiety undergoes internal rotation, leading to torsional splittings of all rotational transition into doublets. The barrier to internal rotation of the methoxy methyl group was deduced to be 417.819(72) cm^{-1} and 418.059(27) cm^{-1} for the C_1 and the C_s conformer, respectively, essentially the same values as those in methyl alkanoates with shorter alkyl chain, which are methyl acetate, methyl propionate and methyl butyrate. Geometry parameters such as the rotational constants and centrifugal distortion constants could be determined with very high accuracy. Optimisations at different levels of theory were performed for a comparison with the experimental results. The MP2/6-311++G(d,p) level of theory failed to calculate reliable rotational constants to guide the assigment of the C_1 conformer, while the MP2/cc-pVDZ level fully succeeded.

1 Introduction

Methyl valerate (or methyl pentanoate), $C_4H_9COOCH_3$, belongs to the class of fruit esters. Such aliphatic esters play an important role in nature as fruity odorants of different fruits, flowers and wines. Furthermore, they are widely used as components for perfume or aroma in food industry. A reasonable explanation for the structure-odour relation is currently not available. The odour of a substance cannot be predicted by knowing only its chemical formula. A typical example is the blueberry- or pine apple-like odour of ethyl isovalerate [1] while its isomers ethyl valerate and isoamyl acetate smell like green apple [2] and banana [3], respectively. Obviously, not only the composition but also the molecular structures are essential for determining the odour of a substance.

Studies of gas phase structures of fruit esters are therefore an important step towards the investigation of the structure-odour relation, since the sense of smell starts from gas phase molecules. For such structure analyses, the combination of microwave spectroscopy and quantum chemical calculations (QCCs) is an excellent tool [4]. On the one hand, small esters often have sufficient vapour pressure to be transferred easily to the gas phase for a rotational spectroscopic study. On the other hand, they already contain quite a large number of atoms with many possible conformations, and thus the structures optimised by QCCs becomes helpful to start the spectral assignments. This was shown by many previous studies on natural substances such as limonene oxide [5], linalool [6], cinnamaldehyde [7], the terpene perillaldehyde [8], α-D-galactose [9], coffee furanon [10] and coumarin [11].

Systematic investigations on the gas phase structures of a series of acetates have been reported, starting from methyl acetate, CH_3COOCH_3, up to *n*-hexyl acetate, $CH_3COOC_4H_9$, where the alkoxy chain is steadily incremented by one carbon atom [12-17]. The acetyl methyl group **CH_3**CO in all these acetates undergoes internal rotation with an almost invariant barrier height of 100 cm^{-1}. In contrast, the torsional barrier of the acetyl methyl group in linear aliphatic ketones are conformation-dependent. Two different groups of barrier heights around 180 cm^{-1} and 240 cm^{-1} are observed for the "pseudo-C_s" and the C_1 molecular geometry, respectively [18-22]. In methyl alkanoates, the methoxy methyl group COO**CH_3** shows internal rotation with a higher barrier, which is, e.g., 424.581(56) cm^{-1} in methyl acetate (**1**) [12]. A similar barrier of 429.324(23) cm^{-1} was found in methyl propionate (**2**), where the acetyl group of methyl acetate is replaced by a propionyl group [23]. In the cases of two conformers of methyl butyrate (**3**), the barrier height is about 420 cm^{-1} [24]. The molecule numbering is given in Figure 1. We were interested to know whether the barrier height of the methoxy methyl top remains the same for longer alkyl chains at the other side of the carbonyl group. Hence, our investigation on methyl valerate

[a] *Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), CNRS UMR 7583, Université Paris-Est Créteil, Université Paris Diderot, Institut Pierre Simon Laplace, 61 avenue du Général de Gaulle, F-94010 Créteil cedex, France.*
[b] *Institut Universitaire de France (IUF), 1 rue Descartes, 75231 Paris cedex 05, France*
[c] *Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, D-52074 Aachen, Germany.*
† Corresponding author. Email: lam.nguyen@lisa.u-pec.fr.
†† For Wolfi, passed away before publication.
Electronic Supplementary Information (ESI) available: Cartesian coordinates, results of the basis set variation, Fourier coefficients and potential energy curves, lists of fitted frequencies along with their residuals, correlation matrices. See DOI: 10.1039/x0xx00000x

(**4**) fits well in this series of methyl alkanoates, focusing on two aspects: the internal dynamics and the structural studies on aliphatic alkyl chains. We will report on the conformational landscape of methyl valerate and the internal rotation of the methoxy methyl group investigated by microwave spectroscopy with support from quantum chemical calculations.

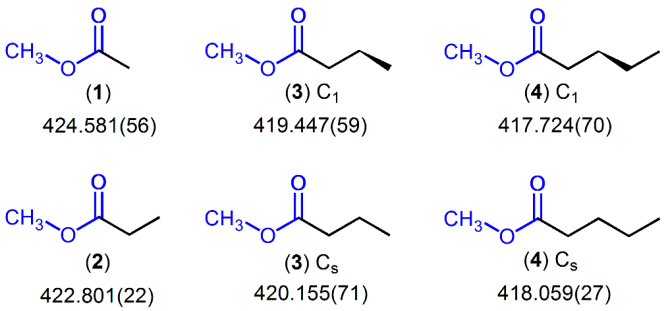

Figure 1 Conformational structures of methyl alkanoates and their respective barrier to internal rotation (in cm^{-1}) of the methoxy methyl group: (**1**) methyl acetate [12], (**2**) methyl propionate [23], (**3**) methyl butyrate [24] and (**4**) methyl valerate (this work). For methyl propionate (**2**), the given value differs from the value of 429.32 cm^{-1} reported in Ref. [23] (see Section 4). Note that for the C_1 conformer of methyl butyrate (**3**) and methyl valerate (**4**), the enantiomeric form with the methyl or ethyl group, respectively, pointing away from the reader is not drawn, but equally probable.

2 Quantum chemical calculations

2.1 Conformational analysis

All QCCs were first carried out at the MP2/6-311++G(d,p) level of theory using the *Gaussian 16* package [25]. We chose this combination of method and basis set, because it provided reasonable rotational constants to support the spectral assignment in many previous studies [26-29]. From the theoretical work of Oki and Nakanishi [30] and some of our own investigations [31,32] we know that *syn* esters (called *cis* in Ref. [30-32]) are more than 20 $kJ{\cdot}mol^{-1}$ higher in energy than *anti* esters (called *trans* in Ref. [30-32]) and cannot be observed under our measurement conditions in the molecular jet where the rotational temperature is very low. Therefore, we only consider *anti* esters in the present study. In total, 27 starting geometries were created by setting each of the dihedral angles $\vartheta_1 = \angle(C_{11},C_8,C_1,O_3)$, $\vartheta_2 = \angle(C_{14},C_{11},C_8,C_1)$ and $\vartheta_3 = \angle(C_{17},C_{14},C_{11},C_8)$ to 180°, 60°, and −60° (for atom numbering see Figure 2). Optimizations yielded 11 conformers, which are confirmed as true minima by harmonic frequency calculations. Their Cartesian coordinates are given in Table S-1 in the Supplementary Material. The rotational constants, dipole moment components, and energies including zero-point corrections relative to the lowest energetic conformer are summarized in Table S-2. Conformers VIII-XI are more than 4.5 $kJ{\cdot}mol^{-1}$ higher in energy than conformer I and are not expected to be present in the experimental spectrum under our molecular jet conditions. Therefore, we will not further consider them. In all conformers, except conformer V, which is illustrated on the left of Figure 2, the *n*-butyl chain is not straight but tilts out of the COOC plane. They belong to the point group C_1. This also holds true for the lowest energy conformer I, depicted on the right of Figure 2.

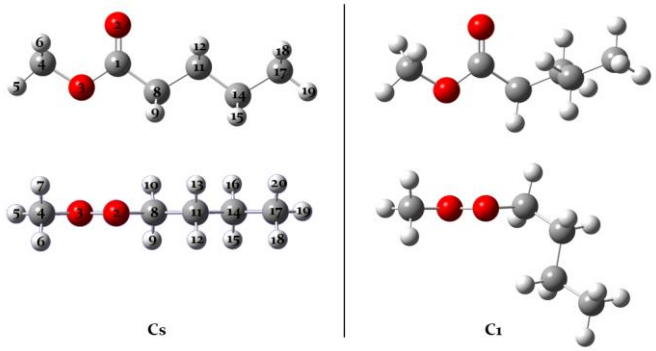

Figure 2 The optimized structures of the two assigned conformers of methyl valerate. Left hand side: the C_s conformer (conformer V); right hand side: the C_1 conformer (conformer I). Upper trace: view on the O−CO−C plane; lower trace: view along the O=C bond.

For the C_s conformer V, all dihedral angles ϑ_i (i = 1-3) are almost 180°. In the C_1 conformer I, the angle ϑ_2 of around 67° is typical for a *gauche* arrangement of the γ carbon atom. The angle ϑ_1 of 146.5° is significantly different from 180°, indicating that the entire alkyl chain is tilted out of the OCOC plane by an angle $\Theta = 180° - |\vartheta_1| = 34.5°$, as can be recognized in the lower right sub-figure of Figure 2. Many previous studies on fruit esters like ethyl valerate [2] and alkylbutyrate [33] or ketones like the series of linear aliphatic ketones [18-22] have indicated the same tilt angle Θ caused by the soft degree of freedom when an alkyl chain is attached to a carbonyl group, whereby the angle Θ is reported to be much larger in esters (from 20 to 50°) than in ketones (from 5 to 25°). This seems to be the reason for disagreements between the predicted and experimental rotational constants with differences of up to 15%, and a more complicated spectral analysis.

2.2 Basis set variations

As we shall see in Section 3.3. describing the spectral assignment, the MP2/6-311++G(d,p) level has completely failed in predicting reliable rotational constants to guide the assignment of the C_1 conformer I. To find a better alternative and to study the soft degree of freedom of the ϑ_1 angle (related to the angle Θ), the MP2 method [34], the B3LYP method with Grimme's distortion corrections [35] and with or without Becke-Johnson damping [36], Truhlar's M06-2X [37] and the coupled cluster (CCSD) methods [38] in combination with different Dunning and Pople basis sets were used to re-optimise the molecular structures of the two eventually assigned conformers I and V.

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Table 1. The rotational constants *A*, *B*, *C* (in MHz), dipole moment components μ_a, μ_b, μ_c (in Debye), the dihedral angles ϑ_1, ϑ_2 and ϑ_3 (in degree) and relative energies $E_{rel.}$ (in kJ·mol^{-1}) including zero-point corrections of the 11 *anti* conformers of methyl valerate calculated at the MP2/cc-pVDZ level of theory. All energies are relative to the lowest energy conformer I with its absolute energy of *E* = −385.333770 Hartree. The experimental values are also given for comparison.

Conf.	*A*	*B*	*C*	$\lvert\mu_a\rvert$	$\lvert\mu_b\rvert$	$\lvert\mu_c\rvert$	ϑ_1	ϑ_2	ϑ_3	$E_{rel.}$
I	5063.6	900.8	843.8	0.71	1.30	0.76	179.51	69.24	–166.05	0.00
II	3295.1	1234.8	1164.4	0.05	1.86	0.47	56.00	52.52	64.33	1.84
III	3262.2	1104.7	990.7	0.86	1.05	1.45	178.19	58.76	51.42	2.22
IV	3043.0	1327.3	1119.8	0.34	1.25	1.06	55.87	57.32	–123.11	2.16
V	7473.5	738.8	686.8	0.23	1.69	0.00	180.00	180.00	179.99	2.18
VI	3330.3	1273.8	1139.5	0.08	0.19	1.61	58.44	–79.64	139.43	2.11
VII	4686.6	831.1	758.7	0.98	1.62	0.76	–179.98	178.88	65.34	4.40
VIII	5618.7	827.6	757.6	0.11	1.63	0.41	63.49	175.48	176.40	4.25
IX	4547.2	895.3	825.3	1.02	1.78	0.08	63.34	175.31	66.65	6.36
X	5092.7	878.1	793.0	0.61	1.91	0.39	63.17	177.59	–68.08	6.46
XI	2921.8	1367.6	1243.5	0.64	0.42	1.86	63.50	–71.71	–47.34	4.78
Expt. C_1	**5063.2**	**897.7**	**846.4**							
Expt. C_s	**7545.3**	**739.5**	**688.5**							

The calculated rotational constants along with the differences to the experimental values and the angle Θ are given in Table S-3 and S-4 in the Electronic Supporting Information (ESI). Finally, the MP2/cc-pVDZ level was applied to re-optimise the geometries of all conformers found on the potential energy surface from the conformational analysis. The Cartesian coordinates of the geometries optimized at this level are also available in Table S-1. The rotational constants, dipole moment components and energies relative to that of conformer I are given in Table 1.

2.3 Internal rotation

As mentioned in the introduction, we expect that the methoxy methyl group in methyl valerate undergoes internal rotation with an intermediate barrier height of about 400 cm^{-1} and causes all rotational lines to split into doublets, like in the case of methyl acetate [12], methyl propionate [23] and methyl butyrate [24]. The internal rotation of the alkyl methyl group CH_2CH_3 can be neglected, since a barrier higher than 1000 cm^{-1} is suspected, similar to the situation found in many molecules such as triethyl amine [39] and ethylacetamidoacetate [40]. Consequently, the rotational lines might be broadened, but most likely no resolved splittings due to this large amplitude motion are visible.

The barrier to internal rotation of the methoxy group was calculated for the most stable conformer I at the MP2/6-311++G(d,p) and MP2/cc-pVDZ levels of theory by varying the dihedral angle $\alpha = \angle(H_5, C_4, O_3, C_1)$ in a grid of 10°, while all other structural parameters were allowed to relax. A rotation of only 120° was needed due to the symmetry of the CH_3 group. At both levels, a three-fold potential was observed with a respective V_3 term of 517.7 and 406.3 cm^{-1}. The obtained potential curves are given in Figure S-1 in the ESI. The V_6 contributions are –10.6 and –25.4 cm^{-1}, respectively.

3 Microwave spectroscopy

3.1 Experimental setup

All spectra were recorded in the frequency range 2 – 40 GHz using modified versions of two molecular jet Fourier transform microwave spectrometers as described in Refs. [41,42]. Methyl valerate was purchased from Merck Schuchardt OHG, Hohenbrunn, Germany, with a stated purity of ≥ 99%. A piece of a pipe cleaner was soaked with the substance and placed directly in front of the nozzle. A helium stream at a total pressure of 150 kPa was allowed to flow over the sample at room temperature, and the helium-substance mixture was expanded into the Fabry-Pérot resonator inside the vacuum chamber.

3.2 Measurements

The spectrometers can function in a high resolution mode and a scan mode. At the beginning, a broadband scan in the frequency range of 9.0 – 14.2 GHz was recorded. A section of this spectrum is given in Figure 3. In this mode, a series of overlapping spectra is automatically recorded, and only the line positions are indicated. All lines were remeasured

afterwards at higher resolution where they split into doublets due to the Doppler effect. Figure 4 illustrates a typical spectrum where the Doppler doublets are marked by brackets. The lines are broader than usual, e.g. in comparison with the line width of 12 kHz in allyl acetate [43]. This is probably due to unresolved splittings from the internal rotation of the alkyl methyl group. The line positions of the C_1 conformer can be determined with a measurement accuracy of 3 kHz, calculated from the average line width of about 30 kHz. For the C_s conformer, the lines are even broader than those of the C_1 conformer, and consequently the measurement accuracy increases to about 4 kHz.

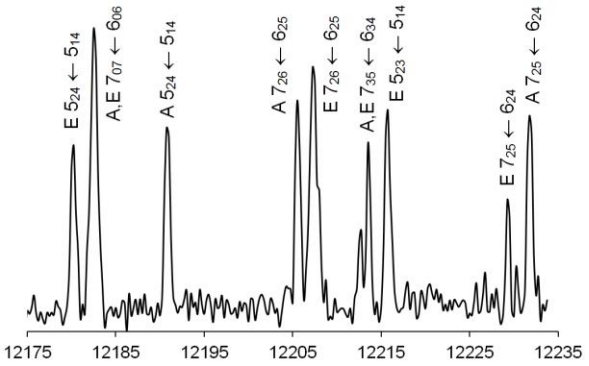

Figure 3 A section of 60 MHz of the broadband scan. The frequencies are given in MHz, intensities in arbitrary unit. The transitions are marked with their corresponding torsional species and quantum numbers J, K_a, K_c. All lines in this scan section belong to conformer I.

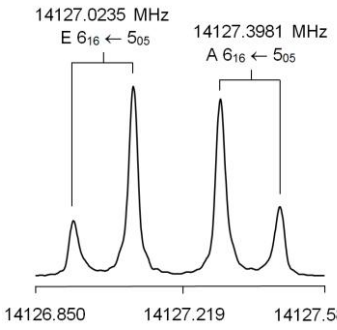

Figure 4 The $6_{16} \leftarrow 5_{05}$ transition of methyl valerate recorded in the high resolution mode. The A-E splitting is 375 kHz. The line widths are approximately 30 kHz. For this spectrum, 44 decays were co-added.

3.3 Spectral assignment

3.3.1. *The C_1 conformer*

We first focused our spectral assignment to conformer I, which was calculated to be the most energetically favourable conformer. At the beginning, the effect of internal rotation was neglected and methyl valerate was treated as a rigid rotor. The rotational constants calculated at the MP2/6-311++G(d,p) level of theory were taken to predict a theoretical spectrum with the *XIAM* program [44]. No agreement between the predicted and the experimental spectrum could be recognized. By shifting the predicted spectrum by approximately 500 MHz, the *R*-branch *a*-type $J = 6 \leftarrow 5$ and $J = 7 \leftarrow 6$ transitions were identified. By trial and error, we also assigned afterwards some *b*- and *c*-type transitions. It was quite surprising that some *Q*-branches are shifted by 2 GHz from their positions in the calculated spectrum. In total, 40 rigid rotor lines in the broadband scan were identified and fitted using three linear combinations $B_J = 1/2\cdot(B + C)$, $B_K = A - B_J$, and $B_- = 1/2\cdot(B - C)$ of the rotational constants to a standard deviation of 264 kHz, which is close to the accuracy of our spectrometer in the scan mode (250 kHz).

As a next step, the internal rotation of the methoxy methyl group was taken into account. Due to this large amplitude motion, each rotational line splits into an A and an E species. The starting value of the V_3 potential was estimated to be 420 cm^{-1}, which is the value found for methyl butyrate [24]. The internal rotor fit also required initial values for the angles δ and ε between the internal rotor axis and the *a*-axis, and between the *b*-axis and the projection of the internal rotor axis onto the *bc*-plane, respectively. These parameters were taken from the geometry of conformer I optimized at the MP2/6-311++G(d,p) level of theory.

The observed A-E splittings are up to a few tens of MHz. We could include 85 A and 83 E species transitions in a fit with a standard deviation of 3.3 kHz using 11 fitted molecular parameters given in Table 2. A comparison between the experimental spectrum and the spectrum reproduced by this fit is indicated in Figure 5. The frequency list of all torsional transitions along with their residuals is available in Table S-5 in the ESI.

Table 2. Molecular parameters of two assigned conformers I (C_1) and V (C_s) of methyl valerate obtained from a fit with the program *XIAM*.

Par.[a]	Unit	C_1	C_s
A	MHz	5063.17500(66)	7545.31936(38)
B	MHz	897.72972(19)	739.47194(21)
C	MHz	846.44127(18)	688.52788(17)
Δ_J	kHz	0.27385(64)	0.0173(15)
Δ_{JK}	kHz	−6.7550(49)	0.1437(54)
Δ_K	kHz	68.78(14)	3.931(24)
δ_J	kHz	−0.01929(32)	0.00196(49)
δ_K	kHz	2.606(81)	
V_3[b]	cm^{-1}	417.724(70)	418.059(27)
$\angle(i,a)$	°	37.784(52)	23.074(30)
$\angle(i,b)$	°	127.698(52)	66.926(30)
$\angle(i,c)$	°	87.8141(25)	90.0[c]
N_A/N_E[d]		85/83	52/52
σ[e]	kHz	3.3	4.1

[a] All parameters refer to the principal axis system. Watson's A reduction in I^r representation was used. The errors in parentheses are in the unit of the last significant digits. [b] The moment of inertia of the methoxy methyl top F_0 is correlated to V_3 and was fixed to 158 GHz in all fits, a value often found for methyl groups and also used in Ref. [24], which corresponds to a moment of inertia of I_α = 3.2 uÅ^2. [c] Fixed due to symmetry. [d] Number of the A (N_A) and E species lines (N_E). [e] Standard deviation of the fit.

3.3.2. *The C_s conformer*

After conformer I was assigned, some lines remained in the scan after all transitions belonging to conformer I had been excluded. From previous investigations on the shorter methyl alkanoate methyl butyrate [24] and other molecules with rich conformational landscape like 1-hexanal [45], octene [46], *N*-allylmethylamine [47] or methyl *n*-propyl sulfide [48], a conformer with C_s structure is often present in the jet cooled microwave spectrum, which is conformer V in the case of methyl valerate. Because only *b*-type transitions were expected to be sufficiently strong, and only three intense rotational transitions of this conformer are located in the broadband scan range, the assignment was challenging, nevertheless possible. We measured 52 A species and 52 E species transitions with $J \leq 9$ and fitted them with the program *XIAM* to a standard deviation of 4.1 kHz. This fit is also given in Table 2; the fitted transitions are listed in Table S-6 in the ESI. Some *c*-type transitions are present in the frequency list, which are all E species lines. It is known that for the E species, *c*-type forbidden transitions can be observed [49], because the quantum numbers K_a and K_c have no meaning for the symmetry of the rotational transitions apart from the A species. For the E species, the K_a and K_c quantum numbers only indicate the order of energy in analogy to the asymmetric top energy level.

4 Results and discussion

While the assignment of the C_s conformer (conformer V) was unambiguous, this was not the case for the C_1 conformer, as illustrated in Figure 6. In the upper diagram of Figure 6, we traced the experimentally deduced rotational constants *A*, *B*, and *C* as straight horizontal lines, and compared them with the calculated values of the seven most stable conformers optimized by QCCs at the MP2/6-311++G(d,p) level of theory, which are given as dots. Conformers I, V, and VII possess reasonable *B* and *C* rotational constants, but conformer V can be excluded immediately because of the presence of *c*-type A species transitions. The *A* rotational constant of conformer I and VII are both close to the experimental value. Nevertheless, the calculated angles of the internal rotor axis with respect to the principal axes of inertia, shown in the lower diagram of Figure 6, confirm that conformer I is assigned, because the methoxy methyl rotor of conformer VII shows a completely different orientation than those deduced from the experiments. A further support for the assignment of conformer I is the similar structure of its alkyl chain $C_4H_9COOCH_3$ to that of the so-called C_1 conformer of ethyl valerate, $C_4H_9COOC_2H_5$, observed under the same measurement conditions [2].

After the spectra of conformers I and V were assigned, a few weak lines remain in the broadband scan (see Figure 5). These signals probably belong to one or several higher energy conformers. However, attempts to find another species were not successful. QCCs yielded 5 other conformers as possible candidates close in energy. Their energy order strongly depends on the level of theory applied for the calculations. In addition, the soft degree of freedom (angle Θ) is also observed for all of these five conformers, which might also cause the same problems of prediction accuracy as found for conformer I. Furthermore, more than one conformer other than conformer I and V may co-exist in the spectrum with only a few strong lines of each visible. As a consequence, the

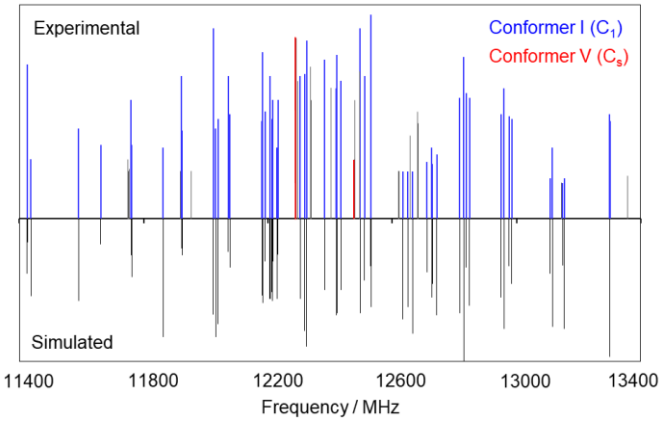

Figure 5 The experimental spectrum in the frequency range from 11400 to 13400 MHz (upper trace) and the spectrum of conformer I reproduced by the *XIAM* fit (lower trace). The A and E species of conformer I are marked in blue and red, respectively. The green lines belong to conformer V; unassigned lines are grey. In this spectrum, only line positions are marked. For a signal to noise ratio, see Figure 3.

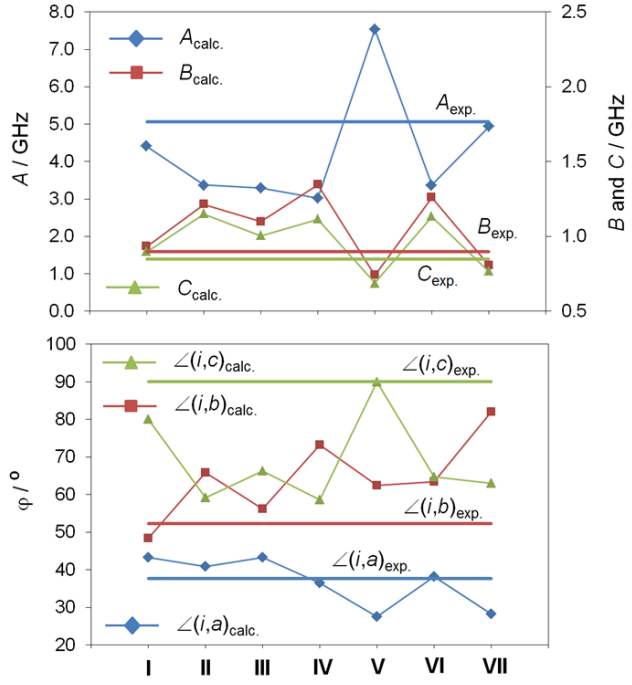

Figure 6 Molecular parameters of the 7 most stable conformers of methyl valerate calculated at the MP2/6-311++G(d,p) level of theory in comparison with experimental results of the C_1 conformer to confirm the assignment of conformer I. In the upper diagram, the experimentally deduced rotational constants ($A_{exp.}$, $B_{exp.}$, and $C_{exp.}$) are visualized as horizontal lines, the calculated values as separated points connected by lines, which are only present for a better tracing. In the lower diagram, the angles between the internal rotor axis and the principal axes φ = ∠(*i*,*n*), *n* = *a*, *b*, *c*, are plotted. The directions of the principal axes were chosen in a way to assure angles between 0° and 90°.

number of lines belonging to one conformer might not be enough to verify any assignment attempt.

The fitted *B* and *C* rotational constants of conformer I differ by −3.9% and −6.0%, respectively, to the values calculated at the MP2/6-311++G(d,p) level of theory (see Table S-3 of the ESI). In particular, the *A* rotational constant drifts by 13.0%, which corresponds to an absolute value of over 650 MHz. This difference is remarkable, because deviations of less than 1% or even better are usually observed [50-54], and the MP2/6-311++G(d,p) level is therefore our most frequently used level due to the reasonable accuracy/calculation time ratio. On the other hand, recent investigations on the C_1 conformers of a series of methyl *n*-alkyl ketone have indicated deviations of up to 5% between the experimental and calculated rotational constants, which can be traced back to the flexibility of up to 25° of the angle Θ upon the internal rotation of the acetyl methyl group which is also attached to the carbonyl bond [19-22]. An even larger deviation of 9 % was found for the C_1 conformer of methyl butyrate for the same reason [24].

Several optimizations using different combinations of methods and basis sets were carried out (see Section 2.2.), revealing that for conformer I, the value of the *A* rotational constant varies in a broad range, whereby the interval is larger in the case of the MP2 method. The *B* and *C* rotational constants are better calculated, though their values differ more significantly from the experimental one in calculations with MP2. Among all calculations, only four yield reasonable agreement between calculated X_e constants and experimental X_0 constants (with X = *A*, *B*, *C*), which are B3LYP-D3/6-311+(+)G(3df,3pd), B3LYP-D3BJ/6-31+G(d,p), and MP2/cc-pVDZ (see Table S-3), whereby the two latter are slightly better than the two former. Figure S-2 in the ESI visualizes the shifts of five *a*-type *R*-branch 6 ← 5, K_a = 0, K_a = 1, and K_a = 2 transitions by reproducing the microwave spectrum using the rotational constants calculated at the MP2/6-311++G(d,p) and MP2/cc-pVDZ levels of theory. Obviously, equilibrium X_e rotational constants calculated at the MP2/6-311++G(d,p) level are not suitable to guide the assignment of conformer I of methyl valerate, even though it yields good results for the C_s conformer V and many other molecules of the same size [26-29,50-54]. It is interesting that the variation of basis sets and methods does not significantly affect the calculated rotational constants of conformer V, which has a C_s symmetry (see Table S-4 in the ESI).

We then applied the B3LYP-D3BJ/6-31+G(d,p) and MP2/cc-pVDZ levels to re-optimize the C_1 conformer of ethyl valerate [2]. The B3LYP-D3BJ level does not deliver as good results for ethyl valerate as it did for methyl valerate, but the MP2/cc-pVDZ level also yield rotational constants with values which are much closer to the experiment ones than any other level reported in Table 2 of Ref. [2] (see Table 3). This level turns out to be a suitable method, with which error compensations accidentally lead to a good agreement between the equilibrium X_e and the experimental X_0 rotational constants of *n*-alkyl valerates. We also mention that purely from a theoretical perspective, MP2/cc-pVTZ should be more accurate. However, the rotational constants predicted at the MP2/cc-pVDZ level are closer to the experimental ones than those calculated at the MP2/cc-pVTZ level due to the X_e-X_0 error compensations.

Moving a further step forward, we applied the MP2/cc-pVDZ level to optimise the C_1 conformer of other esters where similar problems with the soft degree of freedom (called the Θ-problem) have been reported. The results summarized in Table 3 strongly support the conclusion that the MP2/cc-pVDZ level can be recommended as an empirical method not only for *n*-alkyl valerates but also for other related esters with the Θ-problem. However, we underline at this point that currently, a "golden method" does not exist whose error compensations work for all molecules. This highlights the importance of benchmark tests on experimental data.

Table 3. Experimental (Expt.) and rotational constants calculated at the MP2/cc-pVDZ level (Calc., in MHz) with their deviation (in %) of the C_1 conformer of some molecules with the Θ-problem.

Molecule		Expt.	Calc.	Dev.
Methyl butyrate [24]	*A*	6059.3	6046.6	0.2
	B	1421.3	1428.7	0.6
	C	1333.3	1327.7	0.4
Methyl valerate (this work)	*A*	5063.2	5063.6	0.0
	B	897.7	900.8	0.3
	C	846.4	843.8	0.3
Ethyl valerate [2]	*A*	4437.2	4471.3	0.8
	B	612.2	612.6	0.1
	C	595.8	592.8	0.5
Ethyl isovalerate [1]	*A*	4013.5	4040.7	0.7
	B	681.6	680.6	0.1
	C	649.3	644.0	0.8

The lowest energy conformer I of methyl valerate contains the structure of the lowest energy conformer of methyl butyrate [24]. The structure of the alkyl chain is the same as that of the most stable conformer of heptan-2-one where the alkyl chain is bent at the γ carbon position. Probably, the most stable conformer of methyl hexanoate, methyl heptanoate, and longer methyl alkanoate will also contain conformer I of methyl valerate as their sub-structures, similar to the observations found for pentan-2-one, hexan-2-one, heptan-2-one, and octan-2-one [19-22].

The barrier to internal rotation of the methoxy methyl group is 417.724(70) cm^{-1} for the C_1 and 418.059(27) cm^{-1} for the C_s conformer, essentially the same and quite similar to that of methyl acetate [12], methyl propionate [23], and methyl butyrate [24] (see Table 4). We conclude that the length of the alkyl chain and the molecular conformation do not significantly affect the barrier height of the methoxy methyl group. However, a slightly decrease in the barrier height by longer alkyl chain can be recognized from the values given in Table 4. This chain length effect has also been reported for linear aliphatic ketones [22].

Table 4. Experimental barriers V_3 (in cm^{-1}) to internal rotation of methyl alkanoates as well as the dihedral angles (in °) of the alkyl chains calculated at the MP2/cc-pVDZ level of theory.

Molecule	V_3	ϑ_1	ϑ_2	ϑ_3
Methyl acetate [12]	424.6	–	–	–
Methyl propionate [23]	422.8[a]	–	–	180.0
Methyl butyrate [24]	419.4	–	66.3	−147.7
Methyl valerate[b]	417.8	179.5	69.2	−166.0
Ethyl valerate [2]	–	179.5	69.2	−165.7

[a] This value differs from the value of 429.3 cm^{-1} given in ref. [23], where the moment of inertia of the methoxy methyl top F_0 was fixed at 160 GHz. The same data set were fitted again with F_0 = 158 GHz for consistence. [b] This work.

5 Conclusion

The rotational spectrum of methyl valerate was investigated using a combination of microwave spectroscopy and quantum chemistry, revealing two conformers, one with C_1 and the other with C_s symmetry. While many method-basis set combination succeeded to provide predicted rotational constants whose values are close to the experimental ones for the C_s conformer, the soft degree of freedom around the bond connecting the carbonyl group and the alkyl chain found for the C_1 conformer is challenging for quantum chemistry. The MP2/6-311++G(d,p) level of theory failed to calculate reliable rotational constants to guide the assignment of this conformer, while the MP2/cc-pVDZ level succeeded. The rotational constants, centrifugal distortion constants, and internal rotation parameters were determined with very high accuracy using the program *XIAM*. The barrier to internal rotation of the methoxy methyl group is around 418 cm^{-1} for both conformers, indicating that the methoxy methyl torsion is conformation-independent. This value is also essentially the same as in other smaller methyl alkanoates.

Author contributions

Ha Vinh Lam Nguyen: Conceptualization, Investigation, Formal analysis, Visualization, Validation, Writing - Original Draft preparation, Data curation, Supervision, Resources. **Maike Andresen:** Investigation, Formal analysis, Validation, Writing-Review & Editing. **Wolfgang Stahl**: Investigation, Formal analysis, Validation, Writing-Review & Editing, Supervision, Resources.

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