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Maike Andresen, Damian Schöngen, Isabelle Kleiner, Martin Schwell, Wolfgang Stahl, et al.. Internal Rotation of the Acetyl Methyl Group in Methyl Alkyl Ketones: The Microwave Spectrum of Octan-2-one. *ChemPhysChem*, 2020, 21 (19), pp.2206-2216. 10.1002/cphc.202000522 . hal-03182627

**HAL Id: hal-03182627**

**<https://hal.u-pec.fr/hal-03182627>**

Submitted on 26 Mar 2021

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# Internal Rotation of the Acetyl Methyl Group in Methyl Alkyl Ketones: The Microwave Spectrum of Octan-2-one

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**Abstract:** Methyl *n*-alkyl ketones form a class of molecules with interesting internal dynamics in the gas-phase. They contain two methyl groups undergoing internal rotations, the acetyl methyl group and the methyl group at the end of the alkyl chain. The torsional barrier of the acetyl methyl group is of special importance, since it allows for the discrimination of the conformational structure. As part of the series, the microwave spectrum of octan-2-one was recorded in the frequency range from 2 to 40 GHz, revealing two conformers, one with  $C_1$  and one with  $C_s$  symmetry. The barriers to internal rotation of the acetyl methyl group were determined to be  $233.340(28) \text{ cm}^{-1}$  and  $185.3490(81) \text{ cm}^{-1}$ , respectively, confirming the link between conformation and barrier height already established for other methyl alkyl ketones. Extensive comparisons to molecules in the literature were carried out, and a small overview of general trends and rules concerning the acetyl methyl torsion is given. For the hexyl methyl group, the barrier height is  $973.17(60) \text{ cm}^{-1}$  for the  $C_1$  conformer and  $979.62(69) \text{ cm}^{-1}$  for the  $C_s$  conformer.

## 1. Introduction

Methyl groups in molecules might undergo internal rotation. If the barrier hindering this torsion is sufficiently low, the torsional motion becomes feasible and the microwave spectrum of the molecule exhibits splittings of all rotational lines, whereas the barrier height is a characteristic parameter to quantify this effect. In many cases, its value is caused by structural aspects and functional groups of the molecule, making the internal rotor a spectroscopic “detector” of the structure. To explore this link between structural configuration and barrier in ketones, investigations on a series of saturated methyl *n*-alkyl ketones, including butan-2-one,<sup>[1]</sup> pentan-2-one,<sup>[2]</sup> hexan-2-one,<sup>[3]</sup> and heptan-2-one<sup>[4]</sup>, have been performed.

At least two conformers are present in the microwave spectra of all methyl alkyl ketones: One features a  $C_s$  structure, where all heavy atoms are located in a symmetry plane; the other exhibits  $C_1$  symmetry, where the  $\gamma$ -carbon atom of the alkyl chain bends out of the  $C-(C=O)-C$  plane to a synclinal position. Only butan-2-one forms the exception to the series with just the  $C_s$  conformer being identified.<sup>[1]</sup> Connecting the conformational structure to the barrier height of the acetyl methyl group, a symmetry classification with two classes has been proposed.

Conformers of the  $C_1$  class always show a barrier to internal rotation of approximately  $240 \text{ cm}^{-1}$ , while the conformers of the  $C_s$  class exhibit barrier heights around  $180 \text{ cm}^{-1}$ .<sup>[2-4]</sup> In this work, the situation in ketones containing an acetyl methyl group will be further examined.

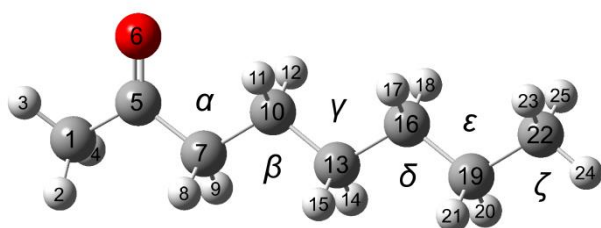
The two main factors determining the value of a rotational barrier are electrostatic and steric effects. While different conformations possess almost the same barrier height in e.g. *n*-alkyl acetates,<sup>[5-10]</sup> the double bond in  $\alpha,\beta$ -unsaturated acetates<sup>[11-13]</sup> augments the torsional barrier of the acetyl methyl group from around  $100 \text{ cm}^{-1}$  found for *n*-alkyl acetates to  $135 \text{ cm}^{-1} - 150 \text{ cm}^{-1}$ . As another example, the steric hindrance of the bulky *tert*-butyl group has been reported to increase the torsional barrier of *tert*-butyl acetate from the value of approximately  $100 \text{ cm}^{-1}$  for other acetates to  $111 \text{ cm}^{-1}$ .<sup>[14]</sup>

Apart from electrostatic and steric effects, the length of the alkyl chain at the other side of the carbonyl group might also affect torsional methyl barriers. The barriers to internal rotation of the acetyl methyl group observed for methyl *n*-alkyl ketones previously studied<sup>[2-4]</sup> suggest a trend: The longer the alkyl chain, the lower the barrier. Moreover, there is a tendency for a plateau curve, i.e. after the alkyl chain is sufficiently long, the barrier remains at a constant value. We were interested to find the limit of the plateau curve and decided to extend the series by studying octan-2-one, also called methyl hexyl ketone. As changes of the barrier heights induced by the alkyl chain length are rather small, the methyl alkyl ketone series is ideally suitable to study this effect because in the three previous investigations on pentan-2-one,<sup>[2]</sup> hexan-2-one,<sup>[3]</sup> and heptan-2-one<sup>[4]</sup> similar sets of parameters have been consistently applied. Since the values of the torsional barriers are quite sensitive to the set of parameters in use, this enables a reliable comparison. To our knowledge, systematic investigations on this chain length effect are not yet available, but there are some two-point data sets hinting at it. In methyl alkynoates the two examples are methyl propionate ( $429.324(23) \text{ cm}^{-1}$ )<sup>[15]</sup> and methyl butyrate ( $420.155(71) \text{ cm}^{-1}$  for the (a,a) and  $419.447(59) \text{ cm}^{-1}$  for the (g $\pm$ ,a) conformer).<sup>[16]</sup> For alkynyl alcohols, there are the examples of 3-pentyn-1-ol ( $9.46 \text{ cm}^{-1}$ )<sup>[17]</sup> and 4-hexyn-3-ol ( $7.16 \text{ cm}^{-1}$ ).<sup>[18]</sup>

## 2. Quantum Chemical Calculations

### 2.1. Geometry Optimizations

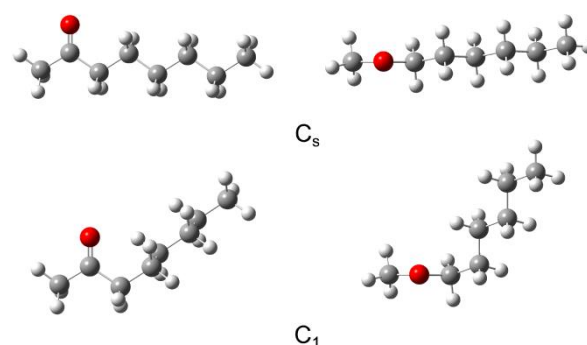
Octan-2-one with its long hexyl chain supports a large number of conformational structures. The conformational landscape is defined by five dihedral angles:  $\theta_1 = \angle(C_1, C_5, C_7, C_{10})$ ,  $\theta_2 = \angle(C_5, C_7, C_{10}, C_{13})$ ,  $\theta_3 = \angle(C_7, C_{10}, C_{13}, C_{16})$ ,  $\theta_4 = \angle(C_{10}, C_{13}, C_{16}, C_{19})$ , and  $\theta_5 = \angle(C_{13}, C_{16}, C_{19}, C_{22})$ . The atom numbering is given in Figure 1. By setting each of the  $\theta_i$  values ( $i = 1 - 5$ ) to  $\pm 60^\circ$  and  $180^\circ$ ,  $3^5 = 243$  staggered starting geometries can be created for optimizations to locate the energy minima. To diminish calculation time, only the energetically most favorable conformers will be focused on, as they are the ones expected to be present under the measurement conditions described in the Experimental Section. From previous studies, we know that the energetically lowest conformers of longer methyl alkyl ketones always contain the conformers of the shorter ones as sub-structure. For example, the  $C_1$  conformer of hexan-2-one<sup>[3]</sup> contains the  $C_1$  conformer of pentan-2-one.<sup>[2]</sup> Based on the two conformers identified for heptan-2-one,<sup>[4]</sup> called the  $C_s$  and the  $C_1$  conformer, the geometry optimizations could hence be reduced to two calculations.



**Figure 1.** Atom numbering of octan-2-one. The hydrogen atoms are white, carbon atoms grey, and the oxygen atom is red. The carbon atom position of the hexyl chain is labeled with Greek letters (see Section 5).

For the  $C_s$  configuration, all starting  $\theta_i$  values of octan-2-one were set to  $180^\circ$ . In the case of the  $C_1$  conformer,  $\theta_2$  was set to  $-60^\circ$ , while the other initial angles were also set to  $180^\circ$ . Optimizations were performed at the MP2/6-311++G(d,p) level of theory using the *Gaussian09* package.<sup>[19]</sup> The optimized geometries are shown in Figure 2. Frequency calculations confirm them to be true minima and not saddle points. The two obtained conformers both exist as an enantiomeric pair. Their rotational constants, dipole moment components, optimized dihedral angles, and relative energies with and without zero-point corrections are summarized in Table 1. The nuclear coordinates are given in Table S1 in the Supporting Information (SI).

In the case of the  $C_1$  conformer, the  $\gamma$ -carbon ( $C_{13}$ ) of the hexyl chain is in a synclinal position ( $\theta_2 = -70.2^\circ$ ). For the  $C_s$  conformer, all heavy atoms seem to lie in a symmetry plane, but actually they do not. The entire hexyl group is tilted out of the C-(C=O)-C plane by approximately  $10^\circ$  ( $\theta_1 = 169.3^\circ$ ). Therefore, this conformer also exists as an enantiomeric pair consisting of an image and a mirror image. Hereafter, its structure will be referred to as “pseudo- $C_s$ ”. These structural peculiarities have been observed in all other members of the methyl  $n$ -alkyl series as well,<sup>[1]-[4]</sup> and will be discussed in Section 5.1.



**Figure 2.** Geometries of the two conformers of octan-2-one optimized at the MP2/6-311++G(d,p) level of theory. Left hand side: View on the C-(C=O)-C plane. Right hand side: View along the O=C bond.

**Table 1.** Rotational constants (in GHz), dipole moment components (in Debye), optimized dihedral angles (in degree) and relative energies without and with zero-point corrections (in  $\text{kJ mol}^{-1}$ ) of the two assigned conformers of octan-2-one calculated at different levels of theory.

	$C_1$ Conformer			$C_s$ Conformer		
	MP2	B3LYP	Exp. <sup>[a]</sup>	MP2	B3LYP	Exp. <sup>[a]</sup>
<b>A</b>	3.962	4.147	4.184	6.261	6.332	6.308
<b>B</b>	0.536	0.518	0.528	0.438	0.433	0.438
<b>C</b>	0.517	0.500	0.508	0.417	0.412	0.417
$ \mu_a $	1.00	0.85		0.28	0.28	
$ \mu_b $	2.05	2.01		3.28	3.28	
$ \mu_c $	2.23	1.78		0.14	0.15	
$\theta_1$	161.6	165.9		169.3	174.9	
$\theta_2$	-70.2	-72.9		178.8	179.2	
$\theta_3$	178.9	179.7		179.7	-179.8	
$\theta_4$	179.4	179.7		179.8	180.0	
$\theta_5$	179.8	179.6		179.9	-179.9	
<b>E</b>	0.00 <sup>[b]</sup>	0.64 <sup>[d]</sup>		2.59 <sup>[b]</sup>	0.00 <sup>[d]</sup>	
<b>E<sub>ZPE</sub></b>	0.00 <sup>[c]</sup>	1.21 <sup>[e]</sup>		1.76 <sup>[c]</sup>	0.00 <sup>[e]</sup>	

[a] Rotational constants obtained from the *XIAM(1Top)* fit, see Table 2 in Section 3. [b] Referring to the absolute energy  $E = -388.635634$  Hartree of the  $C_1$  conformer. [c] Referring to the zero-point corrected energy  $E = -388.406884$  Hartree of the  $C_1$  conformer. [d] Referring to the absolute energy  $E = -389.840232$  Hartree of the  $C_s$  conformer. [e] Referring to the zero-point corrected energy  $E = -389.615084$  Hartree of the  $C_s$  conformer.

### 2.2. Basis Set Variation

The MP2/6-311++G(d,p) level of theory has been chosen for the geometry optimizations, since it has provided a good balance between speed of calculation and reliability in predicting rotational constants for assignment purposes in a variety of molecules, as shown in many of our own investigations<sup>[20]-[22]</sup> and studies in the literature.<sup>[23]-[25]</sup> Nevertheless, for methyl  $n$ -alkyl ketones,<sup>[2]-[4]</sup> especially their  $C_1$  conformers, the accuracy of the

rotational constants predicted at this level does not satisfy the experimental requirements which are crucial for a successful assignment of the microwave spectrum (see Section 3). Therefore, geometry optimizations were repeated applying different combinations of methods and basis sets to find better alternatives. The calculated rotational constants of the  $C_1$  and the  $C_s$  conformer are given in Table S2 and Table S3 of the SI, respectively. The results of the calculations at the B3LYP/6-311++G(d,p) level of theory are also given in Table 1, since it was used for the other methyl alkyl ketones previously studied as well.<sup>[1]-[4]</sup>

### 2.3. Internal Rotation

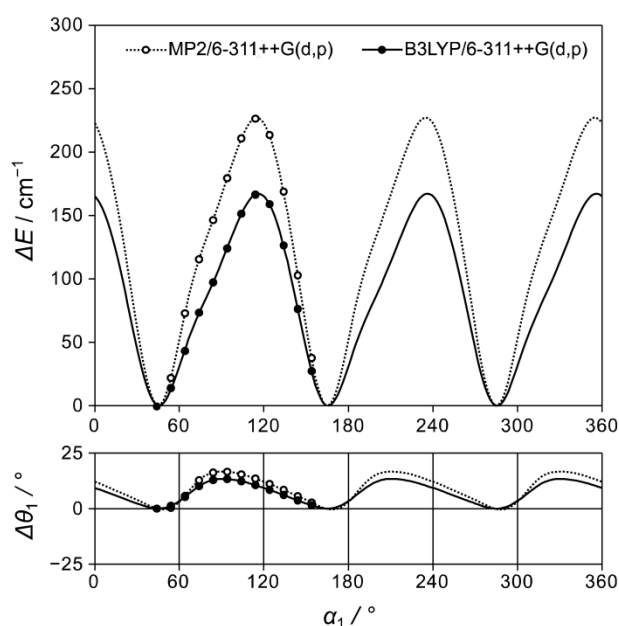
In octan-2-one, the acetyl methyl group  $\text{CH}_3(\text{CO})-$  and the methyl group at the end of the hexyl chain  $-\text{C}_5\text{H}_{10}\text{CH}_3$ , hereafter called hexyl methyl group, both undergo internal rotation, causing each rotational transition to split into five torsional species. These species are labeled as  $\sigma_1\sigma_2 = (00), (01), (10), (11), \text{ and } (12)$ .<sup>[26]</sup>  $\sigma_1$  refers to the acetyl and  $\sigma_2$  to the hexyl methyl group. The numbers  $\sigma = 0, 1, 2$  are equivalent to the respective  $A$ ,  $E_a$ , and  $E_b$  symmetry species of the  $C_3$  group.<sup>[27]</sup>

To calculate the barrier to internal rotation of the acetyl methyl group, the dihedral angle  $\alpha_1 = \angle(\text{H}_2, \text{C}_1, \text{C}_5, \text{C}_7)$  was varied in a grid of  $10^\circ$ , while all other geometry parameters were optimized at the MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p) level of theory. A variation of  $\alpha_1$  of more than  $120^\circ$  was not necessary due to the symmetry of the methyl group. The obtained energies were then parametrized with a one-dimensional Fourier expansion. For the hexyl methyl group, the same procedure was applied for the dihedral angle  $\alpha_2 = \angle(\text{C}_{16}, \text{C}_{19}, \text{C}_{22}, \text{H}_{24})$ . The Fourier coefficients are given in Table S4 in the SI.

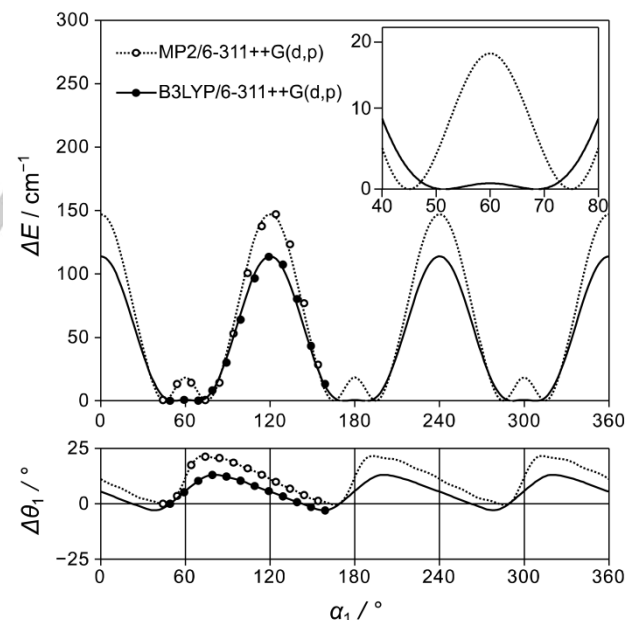
#### 2.3.1. Acetyl Methyl Group

As illustrated in Figure 3, the energy curve of the  $C_1$  conformer shows an expected threefold potential for the internal rotation of the acetyl methyl group. Nevertheless, the shape of this curve is not symmetric. This can be traced back to an oscillation of the entire hexyl group upon rotation of the acetyl methyl group, as depicted with the deviations of the dihedral angle  $\theta_1$  in the lower trace of Figure 3. This observation indicates a certain degree of flexibility of the hexyl chain about the  $\text{C}_5-\text{C}_7$  bond. Higher order terms are included in the parametrization of the energy curve and the estimated barriers to internal rotation are  $227.3 \text{ cm}^{-1}$  and  $167.2 \text{ cm}^{-1}$  with the MP2 and B3LYP methods, respectively.

Figure 4 shows the respective potential energy curve of the  $C_s$  conformer along with the oscillation of its hexyl group ( $\theta_1$ ) upon the rotation of the acetyl methyl group. Here, the oscillation switches between the two enantiomers, which exist due to the "pseudo- $C_s$ " structure of the  $C_s$  conformer (see Section 2.1.). Consequently, the curve shows three-fold shaped double minima with low local barriers at  $\alpha_{\text{max}} = \alpha_1 = 60^\circ, 180^\circ, \text{ and } 300^\circ$ . The double minimum at  $\alpha_1 = 60^\circ$  was explored by reducing the step width of the calculations to  $1^\circ$  (see the inset of Figure 4). Major  $V_6$  contributions were obtained in the Fourier expansions. The local barrier height of  $18.4 \text{ cm}^{-1}$  was calculated with the MP2 method, and a significantly smaller value of  $0.8 \text{ cm}^{-1}$  was obtained with the B3LYP method. The respective values of the global barriers are  $147.1 \text{ cm}^{-1}$  and  $114 \text{ cm}^{-1}$ .



**Figure 3.** Upper diagram: Potential energy curves of the acetyl methyl rotation of the  $C_1$  conformer of octan-2-one obtained by varying the dihedral angle  $\alpha_1$  in a step width of  $10^\circ$ . The energies are calculated at different levels of theory and given relative to the lowest energy conformation. Lower diagram: Changes of the dihedral angle  $\theta_1$  upon the rotation of the acetyl methyl group. The values are given relative to  $161.6^\circ$  (MP2) and  $165.9^\circ$  (B3LYP).



**Figure 4.** Upper diagram: Potential energy curves of the acetyl methyl rotation of the  $C_s$  conformer of octan-2-one obtained by varying the dihedral angle  $\alpha_1$  in a step width of  $10^\circ$ . The energies are calculated at different levels of theory and given relative to the lowest energy conformation. Inset: The double minimum between  $\alpha_1 = 40^\circ$  and  $80^\circ$ , where  $\alpha_1$  was varied in a step width of  $1^\circ$ , is depicted in an enlarged scale. Lower diagram: Changes of the dihedral angle  $\theta_1$  upon the rotation of the acetyl methyl group. The values are given relative to  $169.3^\circ$  (MP2) and  $174.9^\circ$  (B3LYP).



### 2.3.2. Hexyl Methyl Group

In contrast to the behavior of the acetyl methyl group, the internal rotation of the hexyl methyl group is quite regular. All potential energy curves show an undistorted threefold shape, as depicted in Figure S1 of the SI, and only small higher order contributions were needed to parameterize them. For the  $C_1$  conformer, the barrier heights predicted at the MP2 and B3LYP levels are  $1057.5\text{ cm}^{-1}$  and  $995.7\text{ cm}^{-1}$ , respectively. The respective values of the  $C_s$  conformer are  $1053.2\text{ cm}^{-1}$  and  $995.4\text{ cm}^{-1}$ .

## 3. Microwave Spectrum

### 3.1. $C_1$ Conformer

To assign the microwave spectrum recorded under the measurement conditions described in the Experimental Section, the internal rotations of both methyl groups were neglected at first, and octan-2-one was considered to be a rigid molecule. The rotational constants of the  $C_1$  conformer obtained at the MP2/6-311++G(d,p) level of theory (see Table 1) were used as input in the *XIAM* code<sup>[28]</sup> to calculate a theoretical spectrum. The predicted spectrum, however, did not match the experimental one. This is a repeatedly occurring problem within the methyl alkyl ketone series, as found in pentan-2-one,<sup>[2]</sup> hexan-2-one,<sup>[3]</sup> and heptan-2-one,<sup>[4]</sup> since the values of the experimentally deduced and calculated rotational constants deviate by up to 5%. In general, quantum chemical calculations yield equilibrium rotational constants  $X_e$  (with  $X = A, B, C$ ), while with microwave spectroscopy rotational constants of the vibrational ground state  $X_0$  are obtained. Nevertheless, a good agreement between  $X_e$  and  $X_0$  is often accidentally achieved at the MP2/6-311++G(d,p) level due to error compensation.<sup>[20]–[25]</sup> This does not apply for the  $C_1$  conformers of methyl alkyl ketones. Good starting values for the rotational constants of octan-2-one can instead be determined with a semi-empirical correction using experimental data of other methyl alkyl ketones, like for example heptan-2-one,<sup>[4]</sup> and the following equation:

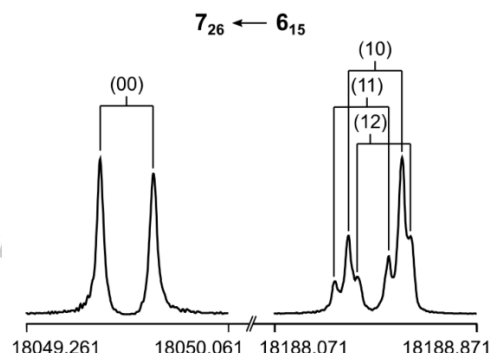
$$X_{\text{start}} = (X_{\text{cal}} \cdot 100) / (\Delta X_{\text{heptan-2-one}} + 100). \quad (1)$$

$X_{\text{cal}}$  are the values of octan-2-one calculated at the MP2/6-311++G(d,p) level of theory.  $\Delta X_{\text{heptan-2-one}}$  is the deviation in percent between the calculated and the experimentally deduced values of the  $C_1$  conformer of heptan-2-one. Using  $X_{\text{start}}$  for predictions of the rotational constants, the (00) species lines of the  $C_1$  conformer of octan-2-one could be assigned.

Considering the effects arising from the internal rotation of the acetyl methyl group, the barrier height of  $233.380(28)\text{ cm}^{-1}$  found for the  $C_1$  conformer of heptan-2-one<sup>[4]</sup> was used as initial value for the  $V_3$  term of octan-2-one. This led to a straight forward assignment of the (10) species transitions, where splittings in the order of several tens to hundreds of MHz were observed. Finally, a dataset containing 380 lines could be fitted to a root-mean-square (rms) deviation of 3.6 kHz. The molecular parameters of the fit are collected in Table 2 in the column named *XIAM(1Top)*. The barrier to internal rotation of the acetyl methyl group is  $233.202(27)\text{ cm}^{-1}$ .

Due to the internal rotation of the hexyl methyl group, all (00) species lines split into the (00) and (01) species and all (10) lines into (10), (11), and (12). These splittings are in the order of

a few kHz, which is close to the resolution limit of 2 kHz of the spectrometers under ideal conditions.<sup>[29]</sup> Hence, they are only resolved for about one quarter of all measured transitions. Otherwise, the lines are either broadened, or the (01), (11), or (12) species lines appear as shoulders of their respective (00) and (10) lines. In some transitions, small additional splittings are observed, probably due to spin-spin and spin-rotation coupling. The attainable measurement accuracy is estimated to be about 3–4 kHz. A typical high-resolution measurement is depicted in Figure 5 for the  $7_{26} \leftarrow 6_{15}$  transition of the  $C_1$  conformer.



**Figure 5.** Typical high resolution measurements of the  $7_{26} \leftarrow 6_{15}$  transition of the  $C_1$  conformer of octan-2-one. The frequencies are given in MHz showing the (00), (10), (11), and (12) species at 18049.6607 MHz, 18188.4716 MHz, 18188.4181 MHz, and 18188.5113 MHz, respectively. The splitting between the (00) and (01) species is not resolved. The brackets indicate splittings caused by the Doppler effect.

The rms deviation of 3.6 kHz of the *XIAM(1Top)* fit is in good agreement with the measurement accuracy. However, it is noteworthy that some branches in the fit show much larger residuals of up to 20 kHz, probably due to missing parameters in the Hamiltonian. To prove the correct assignment, the dataset was refitted using the *BELGI-C<sub>1</sub>* code,<sup>[30]</sup> a program working in the rho axis system. Floating 16 parameters yielded an rms deviation of 2.8 kHz and a barrier height of  $227.78(73)\text{ cm}^{-1}$ . The large residuals observed in the *XIAM(1Top)* fit disappeared. *BELGI* parameters which can be transformed into the principal axis system are also summarized in Table 2. The complete set of fitted parameters is given in Table S5 in the SI.

To include the internal rotation of the hexyl methyl group in the fit, 135 resolved (01), (11), and (12) species lines were added to the *XIAM(1Top)* fit. This *XIAM(2Tops)* fit with an rms deviation of 3.8 kHz is given in Table 2, as well. The barrier heights are  $233.340(28)\text{ cm}^{-1}$  for the acetyl methyl group and  $973.17(60)\text{ cm}^{-1}$  for the hexyl methyl group. The fitted frequencies and the residuals of the *XIAM(1Top)*, *XIAM(2Tops)*, and *BELGI-C<sub>1</sub>* fit are listed in Table S6 in the SI.

### 3.2. $C_s$ Conformer

The assignment of the  $C_s$  conformer followed the same general procedure as that applied for the  $C_1$  conformer. Here, a semi-empirical correction was not necessary, since the rotational constants calculated at the MP2/6-311++G(d,p) level of theory were reasonable starting values. After some cycles of trial and error, several (00) species transitions of *a*- and *b*-type transitions could be assigned. No *c*-type lines were observed, as is expected for a molecule with  $C_s$  symmetry.

**Table 2.** Molecular parameters of the two assigned conformers of octan-2-one. The *BELGI* and *XIAM(1Top)* fits contain only the internal rotation of the acetyl methyl group, while the *XIAM(2Tops)* fits include the internal rotations of the acetyl methyl group and the hexyl methyl group. All parameters refer to the principal axis system. I' representation and Watson's A reduction were used.

Parameter	C <sub>1</sub> Conformer			C <sub>s</sub> Conformer		
	BELGI-C <sub>1</sub> <sup>[a]</sup>	XIAM(1Top)	XIAM(2Tops) <sup>[b]</sup>	BELGI-C <sub>s</sub> <sup>[a]</sup>	XIAM(1Top)	XIAM(2Tops) <sup>[c]</sup>
A / GHz	4.1248(19)	4.18350809(87)	4.18350753(89)	6.30100(16)	6.3084438(13)	6.3084427(13)
B / GHz	0.52955(16)	0.52829755(11)	0.52829782(11)	0.437907(13)	0.437833675(65)	0.437834290(64)
C / GHz	0.50832(26)	0.507655542(98)	0.50765522(10)	0.4171814(14)	0.417060918(53)	0.417060354(53)
$\Delta_J$ / kHz		0.06030(10)	0.06022(11)	0.0059(02)	0.00590(21)	0.00602(21)
$\Delta_{JK}$ / kHz		-1.6630(15)	-1.6615(14)		0.0458(25)	0.0444(24)
$\Delta_K$ / kHz		28.775(21)	28.759(21)		4.821(29)	4.81(26)
$\delta_J$ / kHz		0.005369(39)	0.005465(52)		0.00073(11)	0.00081(10)
$\delta_K$ / kHz		0.350(39)	0.332(40)			
$F_{0,1}$ / GHz	169.5(19)	158.0(fixed)	158.0(fixed)	157.828(48)	158.0(fixed)	158.0(fixed)
$V_{3,1}$ / cm <sup>-1</sup>	227.78(73)	233.202(27)	233.340(28)	185.126(17)	185.1442(79)	185.3490(81)
$\angle(i,a)$ / °	29.46(20)	29.476(36)	29.490(37)	31.717(11)	31.724(10)	31.730(10)
$\angle(i,b)$ / °	97.80(13)	97.79(29)	97.88(29)	121.717(11)	121.724(10)	121.730(10)
$\angle(i,c)$ / °	118.22(22)	118.23(12)	118.22(13)	90.00(fixed)	90.00(fixed)	90.00(fixed)
$D_{p2J,1}$ / MHz		0.08499(17)	0.08506(18)		0.00827(11)	0.00827(11)
$D_{p2K,1}$ / MHz		-3.3938(63)	-3.3977(64)		-0.6317(55)	-0.6346(55)
$D_{p2-,1}$ / MHz		0.018191(80)	0.018238(73)		0.001563(54)	0.001597(56)
$V_{3,2}$ / cm <sup>-1</sup>			973.17(60)			979.62(69)
$N^{[d]}$	380	380	515	244	244	331
$N((00)/(10))^{[e]}$	208/172	208/172	208/172	94/150	94/150	94/150
$N((01)/(11)/(12))^{[e]}$			7/64/64			5/39/43
$\sigma_{rms}^{[f]}$ / kHz	2.8	3.6	3.8	3.5	3.8	3.9

[a] The *BELGI* parameters were transformed from the rho axis system into the principal axis system. [b] The internal rotation parameters of the second rotor are fixed to  $F_{0,2} = 158.0$  GHz,  $\angle(i,b) = 156.92^\circ$ ,  $\angle(i,c) = 87.94^\circ$ , and  $\angle(i,c) = 67.02^\circ$ . [c] The internal rotation parameters of the second rotor are fixed to  $F_{0,2} = 158.0$  GHz,  $\angle(i,b) = 144.22^\circ$ ,  $\angle(i,c) = 54.22^\circ$ , and  $\angle(i,c) = 90.00^\circ$ . [d] Total line number. [e] Line number of the respective species. [f] Root-mean-square deviation of the fit.

The barrier to internal rotation of the acetyl methyl group of 185.469(16) cm<sup>-1</sup> obtained for the C<sub>s</sub> conformer of heptan-2-one<sup>[4]</sup> was used as starting value for octan-2-one, with which the (10) species lines could be straightforwardly assigned. In total, 244 (00) and (10) transitions were fitted with the program *XIAM*, yielding an rms deviation of 3.8 kHz and a  $V_3$  potential of 185.1442(79) cm<sup>-1</sup>. The respective values obtained with the program *BELGI* are 3.5 kHz and 185.126(17) cm<sup>-1</sup>. The results of the fits are also given in Table 2. The 13 floated *BELGI* parameters are collected in Table S5 in the SI. For this conformer, the *BELGI-C<sub>s</sub>* version<sup>[31]</sup> was used, which deals with molecules where the molecular frame to which the rotor is attached has C<sub>s</sub> symmetry. *BELGI-C<sub>s</sub>* does not include parameters associated with imaginary matrix elements, for example  $D_{ac}$ .

The *XIAM(1Top)* fit was extended to the *XIAM(2Tops)* fit by including 87 resolvable (01), (11), and (12) lines. The rms deviation is 3.9 kHz. The barrier heights are 185.3490(81) cm<sup>-1</sup>

for the acetyl and 979.62(69) cm<sup>-1</sup> for the hexyl methyl group. All frequencies and the residuals of the *XIAM(1Top)*, *XIAM(2Tops)*, and *BELGI-C<sub>s</sub>* fits are listed in Table S7 in the SI.

After the assignment of the C<sub>1</sub> and C<sub>s</sub> conformers, only a few lines of very low intensity remained in the broadband scan. They may be transitions of other conformers or caused by impurities, but the line numbers and intensities were not sufficient for another successful identification.

## 4. Discussion

Two conformers could be assigned in the microwave spectrum of octan-2-one. If the molecular parameters of the different fits are compared to each other (see Table 2), the values of the parameters obtained with the *XIAM(1Top)* and *XIAM(2Tops)* fits are very similar, but they differ slightly from those of the *BELGI*

fit. These divergences can be traced back to the different Hamiltonian approaches used by the two codes, and also to the inclusion of higher order parameters in the *BELGI* fits. Substantially, the results agree with each other, and measurement accuracy was reached by all fits.

The calculated rotational constants of the  $C_s$  conformer (see Section 2.2.) are in good agreement with the experimental values (deviations of about 1 % or less). For the  $C_1$  conformer, however, the deviations are much larger. Especially, calculations using the MP2 method yield values of the  $A$  rotational constant up to 5 % lower than the experimental value. This discrepancy between calculation and experiment has been found for other methyl alkyl ketones as well,<sup>[2]-[4]</sup> but also for alkyl esters which are long enough to support a  $C_1$  geometry. For example, deviations of up to 9 % have been reported for methyl butyrate.<sup>[16]</sup> This is not surprising, since the structure of methyl butyrate is very similar to that of pentan-2-one,<sup>[2]</sup> where the acetyl methyl group is exchanged with a methoxy group. In the study on methyl butyrate, Hernandez-Castillo et al. pointed out that the bond between the carbonyl group and the rest of the carbon chain causes most of the problems for the calculations with a wide variety of values found for the corresponding dihedral angle at different levels of theory.<sup>[16]</sup> For methyl alkyl ketones, this dihedral angle, called  $\theta_1$  here, also shows a degree of unexpected flexibility (see the lower diagram of Figure 3 and Figure 4 in Section 2.3.1), and might indeed be responsible for the failure of the calculations. For the  $C_1$  conformer, the best accordance is achieved by using dispersion corrections in combination with polarization functions, but without diffuse functions, as can for example be seen at the B3LYP-D3BJ/6-311(df,pd) level of theory (see Table S2 of the SI). The error compensations at the B3LYP-D3BJ/cc-pVDZ level of theory yield  $X_e$  constants which are in almost exact agreement with the experimental values of both conformers of octan-2-one, and all other methyl alkyl ketones in the series. Though comparing predicted  $X_e$  constants with experimental  $X_0$  constants is not physically meaningful, here, the B3LYP-D3BJ/cc-pVDZ level offers cost-efficient calculations with accidentally good accuracy and is therefore recommended for the assignment of other methyl  $n$ -alkyl ketones with longer alkyl chains.

In the case of the barrier heights, accurate calculations are difficult to achieve, as shown for example in *N*-acetyl alanine methyl ester where differences between the experimentally deduced and the calculated barriers of up to 80 % were observed.<sup>[32]</sup> For octan-2-one, the deviations are about 3 to 40 % and 2 to 9 % for the internal rotation of the acetyl methyl and the hexyl methyl group, respectively (see Section 2.3.).

As mentioned in the preceding paragraphs, finding a quantum chemical method which systematically yields reliable starting values for microwave spectroscopic analyses is a challenging task. In the present work, this problem was circumvented by using available experimental data to correct the calculated rotational constants with a semi-empirical calibration factor (see Section 3.1.). Alternatively, intensity patterns can be modulated and analyzed using strong-field coherence breaking (SFCB), as has been done for methyl butyrate<sup>[16]</sup> and hexan-2-one.<sup>[33]</sup> Other approaches aim at improving the quantum chemical calculations. One example is how basis set superposition errors of the MP2 method can be estimated by the so-called atomic counterpoise method.<sup>[34]</sup> In another example, diffusion quantum Monte Carlo is used to calculate barriers.<sup>[35]</sup>

Nevertheless, more elaborated and consequently more time-consuming and expensive calculations do not guarantee better results, and low-cost levels with error compensations might give the right answers for the wrong reasons. So far, a “golden method” for all molecules and problems is not available. Therefore, any new class of molecules requires its own assessment and benchmark tests to find the best method to use, which can then be applied for all following investigations in the series.

## 5. Methyl Alkyl Ketones: An Overview

### 5.1. Structural Aspects of the Conformations

In this section, the structural aspects of the conformers generally observed in methyl  $n$ -alkyl ketones will be reviewed.<sup>[1]-[4]</sup> The different atom positions of the alkyl chain attached to the carbonyl group are labeled with  $\alpha$ ,  $\beta$ ,  $\gamma$ , etc. (see Figure 1). Tilt angles will be given relative to the all-*trans* conformation, where all  $\theta_i$  dihedral angles are 180° and all heavy atoms lie in a mirror plane.

#### 5.1.1. The $C_s$ or “Pseudo- $C_s$ ” Conformer

Independent of the length of the alkyl chain, one conformer is always present in the gas-phase spectrum of all methyl  $n$ -alkyl ketones, which appears to possess an all-*trans* geometry and is therefore called the  $C_s$  conformer. However, calculations at different levels of theory suggest that the  $\beta$ -carbon, and thereby the entire alkyl chain, is tilted out of the C-(C=O)- $C_\alpha$  plane by about 10° (see Section 2.1.). This “pseudo- $C_s$ ” structure cannot be confirmed nor disproven with the available data sets. As described in Section 3.2. for octan-2-one and observed in general for all other methyl alkyl ketones in the series,<sup>[1]-[4]</sup> no  $c$ -type transitions were identified and the spectrum could be fitted with a satisfactory rms deviation using the *BELGI- $C_s$*  code. Moreover, in the *XIAM* fits the angles between the internal rotor axes and the principal  $c$ -axis were fixed to  $\angle(\hat{h}, c) = \angle(\hat{k}, c) = 90^\circ$ . These are indications for a “true  $C_s$ ” symmetry. Nevertheless, the possibility for a “pseudo- $C_s$ ” structure cannot be excluded either, as a “pseudo- $C_s$ ” conformer might behave like an “effective  $C_s$ ” conformer if the barrier dividing the enantiomeric pair is smaller than the zero-point energy of the tunneling ground state. In a recent investigation on 2-propionylthiophene, where an ethyl group is attached on one side of the carbonyl group and the planar thiophene ring on the other side, Dindic et al. observed a tiny, but non-zero tilt angle of the ethyl group, proving that the ethyl group is not located in the thiophene plane. Using isotopic substitutions, the deduced experimental heavy atom skeleton convincingly confirmed the non-planarity of 2-propionylthiophene.<sup>[36]</sup> Unfortunately, no  $^{13}\text{C}$  isotopologues could be measured in the spectrum of any methyl alkyl ketone in the series. Other molecules exhibiting “pseudo- $C_s$ ” geometries are e.g. methyl neopentyl ketone,<sup>[37]</sup> cat ketone,<sup>[38]</sup> and diethyl ketone.<sup>[39]</sup>

#### 5.1.2. The $C_1$ Conformer

The second type of conformer identified in the microwave spectrum of all methyl alkyl ketones is one with  $C_1$  symmetry and a configuration where the  $\beta$ -carbon is slightly tilted out of the C-(C=O)- $C_\alpha$  plane ( $\theta_1 \approx 160^\circ$ ), while the  $\gamma$ -carbon is in a synclinal position ( $\theta_2 \approx 70^\circ$ ). Butan-2-one is not sufficiently long

to support such a structure.<sup>[1]</sup> In the case of hexan-2-one,<sup>[3]</sup> heptan-2-one,<sup>[4]</sup> and octan-2-one, the supplementary  $\delta$ ,  $\epsilon$ , and  $\zeta$ -carbon atoms are all in *trans* positions ( $\theta_i \approx 180^\circ$ , with  $i = 3, 4, 5$ , respectively).

### 5.1.3. Conformational Stability

It is not clear, whether the  $C_1$  or the  $C_s$  conformer is the most abundant and therefore energetically most favorable structure. Depending on the level of theory in use, the calculated energy orders change (see Table 1), and under our measurement conditions described in the Experimental Section, it is not possible to obtain reliable line intensities for a population ratio analysis. Dipole moment measurements were not performed. Hence, quantitative statements on the conformational stability are not attempted. Qualitatively, both conformers seem to be equally abundant in the spectrum.

“Chemical intuition” would suggest a preference for the  $C_s$  structure. However, similar bent configurations have been observed for a number of molecules where an alkyl chain is attached to a carbonyl group such as *n*-aldehydes<sup>[40]–[43]</sup> and esters like ethyl valerate.<sup>[44]</sup> In a study on methyl butyrate, Hernandez-Castillo et al. determined a population ratio of 59/41 for the (*g* $\pm$ ,*a*) conformer ( $C_1$  conformer equivalent) vs. the (*a*,*a*) conformer ( $C_s$  conformer equivalent).<sup>[16]</sup> There, it has been proposed that the  $C_1$  geometry is stabilized by two weak hydrogen bonds between the oxygen atom of the carbonyl group and (i) one hydrogen atom attached to the  $\gamma$ -carbon and (ii) one hydrogen atom attached to the  $\beta$ -carbon. Such weak hydrogen bonds are also conceivable for the  $C_1$  conformers of the ketone series.

Acetates are molecules where the  $\alpha$ -methylene group of methyl alkyl ketones is exchanged by an  $\alpha$ -oxygen atom, and the carbon chain starts at the  $\beta$ -position. Here, the most abundant conformer shows a different  $C_1$  structure, where the  $\delta$ -carbon and not the  $\gamma$ -carbon is synclinal bent, and all other dihedral angles stay *trans*.<sup>[7]–[10]</sup> It seems that a hydrogen bond between the  $\alpha$ -oxygen and a hydrogen atom attached at the  $\delta$ -carbon stabilizes this conformation of acetates. It is noteworthy that even weak intramolecular interactions, like van der Waals forces, might be strong enough to switch the preference from an all-*trans* to a bent structure, as has been shown for stretched and double layered hairpin conformers of *n*-alkanes with a chain length of at least 16–18 carbons.<sup>[45]–[46]</sup> However, the alkyl chain of methyl alkyl ketones studied so far is not long enough to experience this effect.

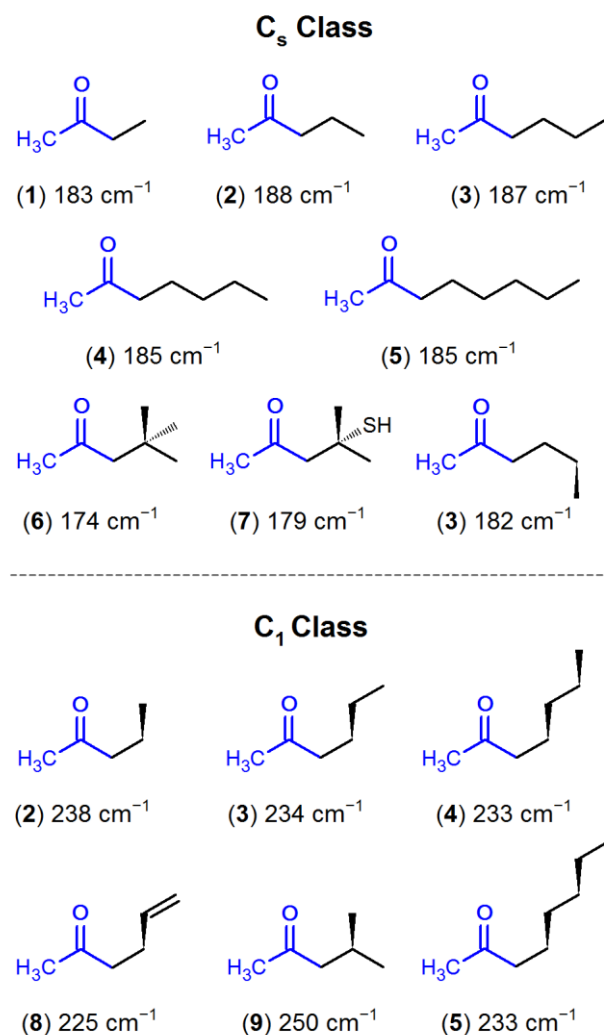
Only in hexan-2-one, a third conformer was observed which features the  $\delta$ -carbon in a synclinal position, while the  $\beta$ -carbon is tilted out of the C–(C=O)–C $_{\alpha}$  plane by  $10^\circ$ , like it is the case for the  $C_s$  conformer.<sup>[3]</sup> This structure, hereafter called  $C_1$ - $\delta$ , is clearly less favorable than that of the  $C_1$  and  $C_s$  conformers.

## 5.2. Acetyl Methyl Internal Rotation

### 5.2.1. Structure-Barrier Dependence

Torsional barriers of the acetyl methyl group in ketones can be categorized into two classes. The first class contains all  $C_s$  conformers of the methyl *n*-alkyl series,<sup>[1]–[4]</sup> and is therefore called the “ $C_s$  class”. As depicted in Figure 6, the barrier height is always about  $180\text{ cm}^{-1}$  and firmly linked to the presence of a “pseudo- $C_s$ ” structure (see Section 5.1.1.). Other molecules belonging to this class are methyl neopentyl ketone (6),<sup>[37]</sup> cat

ketone (7),<sup>[38]</sup> and the  $C_1$ - $\delta$  conformer of hexan-2-one (3)<sup>[3]</sup> (for molecule numbering, see Figure 6). The second class encloses all  $C_1$  conformers of the methyl alkyl ketone series,<sup>[2]–[4]</sup> therefore called the “ $C_1$  class”, as well as allyl acetone (8)<sup>[47]</sup> and methyl isobutyl ketone (9).<sup>[48]</sup> The barrier height is approximately  $240\text{ cm}^{-1}$ , which connects to a structure with a synclinal  $\gamma$ -carbon. In summary, the barrier to internal rotation of the acetyl methyl group can be linked to structural characteristics of the alkyl chain, making the acetyl methyl group a spectroscopic “detector” of the molecular conformation.



**Figure 6.** Conformational structures of ketones in the  $C_s$  and  $C_1$  class, as well as their respective barrier to internal rotation of the acetyl methyl group (rounded to an accuracy of  $1\text{ cm}^{-1}$ ): (1) butan-2-one,<sup>[1]</sup> (2) pentan-2-one,<sup>[2]</sup> (3) hexan-2-one,<sup>[3]</sup> (4) heptan-2-one,<sup>[4]</sup> (5) octan-2-one (this work), (6) methyl neopentyl ketone,<sup>[37]</sup> (7) cat ketone,<sup>[38]</sup> (8) allyl acetone,<sup>[47]</sup> and (9) methyl isobutyl ketone.<sup>[48]</sup>

In Table 3 a selection of ketones containing an acetyl methyl group is presented. These ketones neither fit in the  $C_1$  nor in the  $C_s$  class, because either the torsional barrier or the molecular structure does not match.



**Table 3.** A collection of ketones containing an acetyl methyl group and their respective barriers to internal rotation.

Molecule	Barrier Height <sup>[a]</sup>	Ref.
<b>Acetone Class</b>		
Acetone	242 cm <sup>-1</sup>	[54]
Trifluoroacetone	259 cm <sup>-1</sup>	[56]
Acetone + Ne <sup>[b]</sup>	259 cm <sup>-1</sup>	[59]
Acetone + Ar <sup>[b]</sup>	260 cm <sup>-1</sup>	[60]
Difluoroacetone	261 cm <sup>-1</sup>	[55]
Trifluoroacetone + H <sub>2</sub> O <sup>[c]</sup>	275 cm <sup>-1</sup>	[57]
<b>Mesomeric Class</b>		
<i>sp</i> - $\beta$ -Ionone <sup>[d]</sup>	341 – 343 cm <sup>-1</sup>	[53]
<i>sp</i> - $\alpha$ -Ionone <sup>[d]</sup>	356 – 360 cm <sup>-1</sup>	[53]
<i>sp</i> -Acetyl Vinyl Ketone	377 cm <sup>-1</sup>	[52]
<i>ap</i> - $\beta$ -Ionone <sup>[d]</sup>	427 – 437 cm <sup>-1</sup>	[53]
<i>ap</i> -Acetyl Vinyl Ketone	434 cm <sup>-1</sup>	[52]
<i>ap</i> - $\alpha$ -Ionone <sup>[d]</sup>	439 – 455 cm <sup>-1</sup>	[53]
<b>Phenyl Class</b>		
Acetovanillone <sup>[d]</sup>	552 – 622 cm <sup>-1</sup>	[51]
6-Hydroxy-3-methoxyacetophenone <sup>[d]</sup>	588 – 612 cm <sup>-1</sup>	[51]
Acetophenone + H <sub>2</sub> O <sup>[c]</sup>	589 cm <sup>-1</sup>	[50]
4-Methylacetophenone	594 cm <sup>-1</sup>	[49]
Acetophenone	627 cm <sup>-1</sup>	[50]
<b>Not yet classified</b>		
Acetylacetone	57 cm <sup>-1</sup>	[61]
Pinacolone	122 cm <sup>-1</sup>	[62]
<i>cis</i> -2-Acetyl-5-methylfuran	213 cm <sup>-1</sup>	[63]
Phenylacetone	238 cm <sup>-1</sup>	[64]
<i>trans</i> -2-Acetyl-5-methylfuran	308 cm <sup>-1</sup>	[63]
Diacetyl	319 cm <sup>-1</sup>	[58]
Diacetyl + H <sub>2</sub> O <sup>[c]</sup>	344 cm <sup>-1</sup>	[58]
Cyclopropyl Methyl Ketone	413 cm <sup>-1</sup>	[65]

[a] All values are rounded to an accuracy of 1 cm<sup>-1</sup>. [b] Barrier height of a noble-gas complex. [c] Barrier height of a monohydrated water complex. [d] A range is given, since different orientations of functional groups other than the acetyl methyl group lead to different conformers with slightly different barrier heights.

Recently, Herbers et al. extended the “two-class” concept of the acetyl methyl barriers in ketones to include a “phenyl class”,<sup>[49]</sup> There, a phenyl ring instead of an alkyl chain is attached on one side of the carbonyl group. The barrier heights

are between 550 cm<sup>-1</sup> and 630 cm<sup>-1</sup>. Members of this class are acetophenone,<sup>[50]</sup> 4-methylacetophenone,<sup>[49]</sup> acetovanillone,<sup>[51]</sup> and 6-hydroxy-3-methoxyacetophenone.<sup>[51]</sup> A “mesomeric class” enclosing methyl vinyl ketone<sup>[52]</sup> and ionone<sup>[53]</sup> might also exist, since both molecules contain an unsaturated  $\alpha,\beta$ -bond in their alkyl chains. This class needs a division in an antiperiplanar (*ap*) and a synperiplanar (*sp*) sub-class with respective barriers of about 430 cm<sup>-1</sup> and 350 cm<sup>-1</sup>. Acetone,<sup>[54]</sup> difluoroacetone,<sup>[55]</sup> and trifluoroacetone<sup>[56]</sup> are candidates for an “acetone class” with barrier heights of approximately 250 cm<sup>-1</sup>. Complexation with water<sup>[50],[57],[58]</sup> or noble gases<sup>[59],[60]</sup> changes the barrier by less than 40 cm<sup>-1</sup>. Further systematic investigations will be needed to fully understand the acetyl methyl torsion in ketones and to propose new classifications. However, the present overview might already serve as guideline for future studies.

## 5.2.2. Conformational Effects

### 5.2.2.1. Steric or Electrostatic Effects?

As described in Section 5.2.1., the acetyl methyl group functioning as an internal rotor is a spectroscopic “detector” for the molecular structure. However, the essential questions remain: What exactly is detected by the internal rotation? Steric or electrostatic interactions? We assume that the impact of the latter is much greater, and that the acetyl methyl group can “read” the electrostatic environment on the other side of the carbonyl group. This hypothesis is based on a number of observations, whereas also substance classes other than ketones are taken into consideration:

(i) Methyl neopentyl ketone (molecule (6) in Figure 6) exhibits a “pseudo-C<sub>s</sub>” structure and a methyl group at the same position as the  $\gamma$ -carbon of a C<sub>1</sub> conformer. The steric hindrance of the  $\gamma$ -carbon should put the molecule in the “C<sub>1</sub> class”, but the acetyl methyl barrier is 174.11(27) cm<sup>-1</sup>,<sup>[37]</sup> and methyl neopentyl ketone belongs to the “C<sub>s</sub> class”. The electrostatic characteristic of the “pseudo-C<sub>s</sub>” geometry is the decisive factor.

(ii) Ketones of the “phenyl class” show barrier heights of around 600 cm<sup>-1</sup> (see Table 3),<sup>[49]</sup> which is much higher than the values of 180 cm<sup>-1</sup> and 230 cm<sup>-1</sup> found for the C<sub>s</sub> and C<sub>1</sub> class, respectively. The reason is probably  $\pi$ -electron conjugation between the carbonyl group and the phenyl ring, indicating the important role of electrostatic interactions on the acetyl methyl torsion in ketones.

(iii) If the electrostatic environment in proximity to the carbonyl group is changed by the presence of an oxygen atom attached to the carbonyl group, as it is for example the case for methyl alkanoates and acetates, the barrier is almost unaffected by the molecular configuration and thereby steric hindrance of the alkyl chain. In all methyl alkanoates, the barrier to internal rotation of the methoxy methyl group is always around 400 cm<sup>-1</sup>.<sup>[5],[15][16]</sup> In most alkyl acetates, the barrier height of the acetyl methyl group is approximately 100 cm<sup>-1</sup>.<sup>[5]-[10]</sup> Nevertheless, in acetates where the electrostatic surrounding of the oxygen “buffer atom” is influenced by a double bond or a conjugated  $\pi$ -system, e.g. in vinyl acetate<sup>[11]</sup> and butadienyl acetate,<sup>[13]</sup> the barrier height increases to 150 cm<sup>-1</sup>.

(iv) In amides, the carbonyl group is attached to a nitrogen atom and the barriers to internal rotation depend on the degree of substitution at that nitrogen. For acetamide (CH<sub>3</sub>(C=O)-NH<sub>2</sub>), a remarkably low barrier of 25 cm<sup>-1</sup> has been found for the acetyl methyl group.<sup>[66]</sup> If one of the hydrogen atoms attached to

the nitrogen atom is substituted, secondary acetamides ( $\text{CH}_3(\text{C}=\text{O})\text{-NHR}$ ) with acetyl methyl barriers of approximately  $70\text{ cm}^{-1}$  are obtained. Examples are *N*-methylacetamide ( $\approx 73\text{ cm}^{-1}$ ),<sup>[67]</sup> *N*-ethylacetamide ( $\approx 73\text{ cm}^{-1}$ ),<sup>[68]</sup> and *N*-*tert*-butylacetamide ( $\approx 66\text{ cm}^{-1}$ ),<sup>[69]</sup> as well as *N*-acetyl alanine methyl ester ( $\approx 65\text{ cm}^{-1}$ )<sup>[32]</sup> and the two conformers of ethylacetamidoacetate ( $\approx 64\text{ cm}^{-1}$  and  $\approx 65\text{ cm}^{-1}$ ).<sup>[70]</sup> It is interesting that the substitution of one hydrogen atom leads to a difference of approximately  $50\text{ cm}^{-1}$  in the barrier height between acetamide and the secondary acetamides. If both hydrogen atoms are substituted ( $\text{CH}_3(\text{C}=\text{O})\text{-NR}_2$ ), the effect is even larger as the barrier height increases by an order of magnitude, e.g. to  $677\text{ cm}^{-1}$  in *N,N*-dimethylacetamide<sup>[71]</sup> and to  $517.04(13)\text{ cm}^{-1}$  and  $619.48(91)\text{ cm}^{-1}$  in the two conformers of *N,N*-diethylacetamide.<sup>[72]</sup> Since the substituents are well-separated from the acetyl methyl group by the amide moiety ( $\text{C}=\text{O})\text{-N}$ , the reasons can only be electrostatic and not steric effects.

(v) Finally, in acetyl halides the bond between the halide and the carbonyl group seems to possess a partially ionic character, causing a special electrostatic environment which induces acetyl methyl barriers of about  $450\text{ cm}^{-1}$ .<sup>[73-76]</sup>

#### 5.2.2.2. Chain Length Effects

Electrostatic and steric interactions are the main reasons behind the structural "detection" of the acetyl methyl rotation. The range of this detection probably extends up to  $\gamma$ -carbon, since the  $\text{C}_1$ - $\delta$  conformer of hexan-2-one belongs to the  $\text{C}_s$  and not the  $\text{C}_1$  class (see Section 5.2.1.).<sup>[3]</sup> However, longer alkyl chains might affect the torsion of a methyl group as well. So far, no systematic investigations on chain length effects have been reported, but there are some two-point data sets hinting that a longer alkyl chain is responsible for a lower barrier to internal rotation. For example, the methoxy methyl barrier of methyl butyrate is  $420.155(71)\text{ cm}^{-1}$  for the (a,a) and  $419.447(59)\text{ cm}^{-1}$  for the (g $\pm$ ,a) conformer,<sup>[16]</sup> clearly lower than the value of  $429.324(23)\text{ cm}^{-1}$  found for methyl propionate.<sup>[15]</sup> Similarly, the barrier of the propionyl methyl group of  $9.46\text{ cm}^{-1}$  found for 3-pentyn-1-ol<sup>[17]</sup> is higher than that of  $7.16\text{ cm}^{-1}$  found for 4-hexyn-3-ol.<sup>[18]</sup>

In the  $\text{C}_s$  class, the torsional barriers of pentan-2-one ( $188.3843(50)\text{ cm}^{-1}$ ),<sup>[2]</sup> hexan-2-one ( $186.9198(50)\text{ cm}^{-1}$ ),<sup>[3]</sup> heptan-2-one ( $185.469(16)\text{ cm}^{-1}$ ),<sup>[4]</sup> and octan-2-one ( $185.1442(16)\text{ cm}^{-1}$ ) (see Table 2) strongly support this assumption: The longer the alkyl chain, the lower the barrier. However, beyond a certain molecule length, chain length effects are no longer observed and a plateau of the values is reached. For methyl alkyl ketones, this limit seems to be at the  $\zeta$ -carbon position, as the barrier height is almost unchanged in heptan-2-one and octan-2-one. It should be noted that the scale of these chain length effects is rather small, and that the barrier height is quite sensitive to the set of parameters used in the fitting process. Comparable sets of parameters are essential for a reasonable comparison. For this reason, butan-2-one ( $183.1702(89)\text{ cm}^{-1}$ ) does not match the rest of the series.<sup>[1]</sup> The extraordinary low barrier of  $764.8(16)\text{ cm}^{-1}$  found for the ethyl methyl group requires a two-top model to reproduce the microwave spectrum, whereas for all other methyl *n*-alkyl ketones, a one-top model is sufficient.

For the  $\text{C}_1$  conformer, the chain length detection is almost lost once the alkyl chain is bent at the  $\gamma$ -carbon position. The

acetyl methyl barrier of  $238.145(21)\text{ cm}^{-1}$  observed for pentan-2-one<sup>[2]</sup> decreases noticeably to  $233.5913(97)\text{ cm}^{-1}$  for hexan-2-one,<sup>[3]</sup> and remains largely unchanged at a value of  $233.380(28)\text{ cm}^{-1}$  and  $233.202(27)\text{ cm}^{-1}$  for heptan-2-one<sup>[4]</sup> and octan-2-one (see Table 2), respectively.

#### 5.3. Alkyl Methyl Internal Rotation

The torsional barrier of the hexyl methyl group is about  $1000\text{ cm}^{-1}$  for both conformers of octan-2-one (see Table 2). Similar values are found for the alkyl methyl groups in pentan-2-one,<sup>[2]</sup> hexan-2-one,<sup>[3]</sup> and heptan-2-one.<sup>[4]</sup> In these cases, the splittings arising from the methyl group could be observed, leading to a precise determination of the barrier heights. It is noteworthy that barriers to internal rotation of methyl groups at the end of an alkyl chain are often higher than  $1000\text{ cm}^{-1}$ , which usually inhibits the splittings to be resolved within the resolution of about  $2\text{ kHz}$  of the spectrometer in use, as for example found in studies on triethyl amine<sup>[22]</sup> and diisopropyl ketone.<sup>[77]</sup> In contrast to methyl groups of longer alkyl chains, ethyl methyl groups show a more diverse range of barrier heights. In some cases, such as diethyl amine<sup>[78]</sup> and ethyl acetate,<sup>[6]</sup> resolvable splittings have led to barrier heights of  $1051.74(57)\text{ cm}^{-1}$  and  $1112.3(37)\text{ cm}^{-1}$ , respectively. In other cases, like methyl ethyl ketone,<sup>[1]</sup> diethyl ketone,<sup>[39]</sup> and methyl propionate,<sup>[15]</sup> the internal rotation of the ethyl methyl group possesses a smaller barrier height of about  $800\text{ cm}^{-1}$ . Further conclusions cannot be drawn due to the small set of available data points.

## Conclusion

Two conformers have been identified in the microwave spectrum of octan-2-one, one with a "pseudo- $\text{C}_s$ " symmetry and one with a  $\text{C}_1$  structure where the  $\gamma$ -carbon is in a synclinal position. The barriers to the internal rotation of the acetyl methyl group are  $185.3490(81)\text{ cm}^{-1}$  and  $233.340(28)\text{ cm}^{-1}$ , respectively, confirming the link already established between the torsion of the acetyl methyl group and the conformational structure of methyl *n*-alkyl ketones. In general, the conformers of ketones exhibiting this specific  $\text{C}_s$  or  $\text{C}_1$  structure can respectively be categorized in a  $\text{C}_s$  class with barrier heights of about  $180\text{ cm}^{-1}$  and in a  $\text{C}_1$  class with values of approximately  $240\text{ cm}^{-1}$ . Electrostatic effects play a more decisive role for the acetyl methyl torsion than steric effects do. In addition, there is a small chain length effect observable within the methyl *n*-alkyl ketone series: Longer alkyl chains cause slightly smaller barriers, following the shape of a plateau curve, with the plateau being reached at the chain length of octan-2-one. Moreover, the barriers to the internal rotation of the hexyl methyl group are deduced to be  $973.17(60)\text{ cm}^{-1}$  for the  $\text{C}_1$  and  $979.62(69)\text{ cm}^{-1}$  for the  $\text{C}_s$  conformer. These values are in good agreement with other barriers found for methyl groups terminating various alkyl chains.

## Experimental Section

Octan-2-one was purchased from TCI Europe, Zwijndrecht, Belgium. The stated purity was over 98.0% and no further purification steps were carried out. Two molecular jet Fourier transform microwave spectrometers covering a frequency range from 2 to 40 GHz as described in Ref. [79] and [80] were used to record the microwave

spectrum. A piece of a pipe cleaner soaked in liquid octan-2-one was placed under a helium flow at a pressure of about 200kPa, and the helium-substance mixture was expanded into the Fabry-Pérot cavity of the spectrometers. First, a broadband scan from 9 to 14 GHz with a step width of 0.25 MHz was recorded. After the spectra were assigned, high resolution measurements between 2 and 40 GHz were recorded.

## Acknowledgements

Simulations were performed with computing resources granted by the RWTH Aachen University under project rwth0249. This work was supported by the Agence Nationale de la Recherche ANR (Project ID ANR-18-CE29-0011).

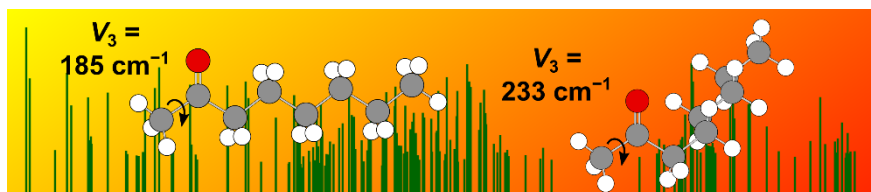
**Keywords:** Ketones • Rotational Spectroscopy • Microwave Spectroscopy • Large Amplitude Motion • Quantum Chemistry

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## Entry for the Table of Contents



Two conformers were identified in the microwave spectrum of octan-2-one. The barriers to internal rotation of the acetyl methyl group could be linked to the respective conformational structure, verifying general trends established for methyl *n*-alkyl ketones and other molecules containing an acetyl methyl group. An overview of methyl *n*-alkyl ketones is given.