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Methyl Internal Rotation in the Microwave Spectrum of *o*-Methyl Anisole

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Abstract The microwave spectrum of *o*-methyl anisole (2-methoxytoluene), CH₃OC₆H₄CH₃, has been measured using a pulsed molecular jet Fourier transform microwave spectrometer operating in the frequency range 2 – 26.5 GHz. Conformational analysis using quantum chemical calculations at the MP2/6-311++G(d,p) level of theory yields only one stable conformer with a C_s structure, which was assigned in the experimental spectrum. A-E splittings due to the internal rotation of the ring methyl group could be resolved and the barrier to internal rotation was determined to be 444.05(41) cm⁻¹. The experimentally deduced molecular parameters such as rotational and centrifugal distortion constants as well as the torsional barrier of the ring methyl group are in agreement with the calculated values.

The gas phase structures of toluene and its derivatives have been the subjects of many rotational spectroscopic studies for decades, especially in the microwave and UV frequency regions. Many investigations by UV spectroscopy have been thoroughly carried out for example in Ref. [1-3], giving information on gas phase structures in the ground and excited electronic states of these molecules. In microwave spectroscopy, halogen atoms,^[4] aldehyde^[5] or alcohol groups^[6] are the most common substituents, also providing sufficiently large dipole moment which eases the measurements. Surprisingly, almost no investigations were performed with the methoxy group as substituent. We are interested in these compounds, because from studies in the literature, we found that the internal rotation of methyl groups attached at the benzene ring is difficult to predict. In toluene, only a V₆ potential is found.^[7] In some cases, the V₃ potential barriers are very low with a large V₆ contribution.^[5] In some other cases, only V₃ contributions remain.^[6] Currently, no study is available to explain systematically this observation.

In the case of mono-substituted methoxy toluenes, which can also be seen as monomethyl substituted anisoles, three relative positions can be ortho, meta, and para, and thus three isomers exist. In the present work, we study the gas phase structure of *o*-methyl anisole (OMA) with a view towards highly

accurate determinations of the barriers to internal rotation. The barrier height of the ring methyl group has only been determined by Alvarez-Valtierra *et al.* with fluorescence spectroscopy, where the authors found for the electronic ground state a V₃ potential of 345 cm⁻¹.^[8]

The structures of substituted anisoles are also interesting: Anisole itself has a planar heavy atom frame^[9] as almost all other related compounds such as phenetole,^[10] *p*-fluoroanisole,^[11] and *p*-anisaldehyde.^[12] However, non-planar structures cannot be excluded, because e.g. for *p*-fluorothioanisole, Lister *et al.* reported on a second isomer with the methylsulfanyl (CH₃-S) group in a nearly perpendicular orientation.^[13] Some other molecules containing a phenyl ring also have non planar structures, as in the cases of phenyl formate^[14] and *N*-phenylformamide.^[15]

Reasonable starting values of molecular parameters such as rotational constants are important for spectral assignment, because reliable predictions of the spectrum considerably simplify the assignment process. Quantum chemistry is a powerful tool for this purpose. The GAUSSIAN09 suite of programs^[16] was employed for all calculations in this work. If not stated otherwise, the MP2/6-311++G(d,p) level of theory is used. We choose this level, because it yields quite reasonable results for some other molecules containing aromatic rings like phenetole,^[10] 2,5-dimethylthiophene,^[17] and 2-acetyl-5-methylfuran.^[18]

Because the rotations of two methyl groups about the C₄-C₁₆ and the O₁₁-C₁₂ bond by varying the dihedral angles $\beta = \angle(\text{C}_5, \text{C}_4, \text{C}_{16}, \text{H}_{19})$ and $\gamma = \angle(\text{C}_3, \text{O}_{11}, \text{C}_{12}, \text{H}_{14})$, respectively, (for atom numbering see Figure 1) do not create new conformations, the conformational preferences of OMA are solely determined by the rotation of the methoxy group about the O₁₁-C₃ bond by varying the dihedral angle $\alpha = \angle(\text{C}_{12}, \text{O}_{11}, \text{C}_3, \text{C}_4)$. A potential curve was calculated where α was varied within a 10° step width while all other geometry parameters were optimized. The calculated energies were parameterized using a Fourier expansion with the corresponding coefficients given in Table S-1 in the Supporting Information. Using these Fourier coefficients, the potential energy curve was drawn as depicted in Figure 2, showing that there is only one possible conformer for OMA at $\alpha = 180^\circ$. This conformer has C_s symmetry, but we note that the minimum of the potential curve is very shallow. Therefore, we recalculate this region within a grid of 1° and also plotted the result in Figure 2 with an enlarged scale.

Full geometry optimizations and frequency calculations were performed afterwards for the minimum (see Figure 1). The Cartesian coordinates are given in Table S-2 in the Supporting Information. We found one imaginary vibrational mode in the harmonic frequency calculations, which is a bending vibration of the phenyl ring. Stating stable planar ring systems as unstable is a well-known behavior found at the MP2/6-311++G(d,p) level of theory, which has been reported for benzene and arenes.^[19]

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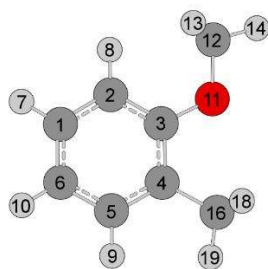


Figure 1. Molecular structure of the only conformer of *o*-methyl anisole optimized at the MP2/6-311++G(d,p) level of theory. The protons H₁₅ and H₁₇ are located behind H₁₃ and H₁₈, respectively.

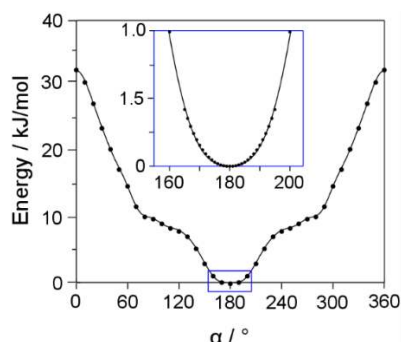


Figure 2. The potential energy curve of *o*-methyl anisole obtained by rotating the methoxy group about the C₃-O₁₁ bond (for atom numbering, see Figure 1) in a grid of 10°. The relative energies with respect to the lowest energy conformation with $E = -385.0454020$ Hartree are given. The minimum region was recalculated in a grid of 1°, as depicted with an enlarged scale.

The only stable conformer of OMA is predicted to possess the rotational constants $A = 2.481$ GHz, $B = 1.559$ GHz, and $C = 0.969$ GHz and the dipole moment components $|\mu_a| = 0.79$ D, $|\mu_b| = 1.01$ D, and $|\mu_c| = 0.00$ D. Consequently, no *c*-type transitions are observable in the microwave spectrum and both, *a*- and *b*-type transitions, are intense.

In spite of its relatively simple structure, the internal dynamic of OMA is challenging. There are two inequivalent methyl internal rotations. The barrier heights of the ring methyl and the methoxy methyl group were calculated by varying the dihedral angles β and γ , respectively, in a grid of 10°. A rotation of 120° was sufficient due to the three-fold symmetry of the methyl groups. We found a V_3 potential of 447.71 cm⁻¹ for the ring methyl and 1118.18 cm⁻¹ for the methoxy methyl group with no significant V_6 contributions. Simple two-top predictions using the program XIAM^[20] indicate that torsional splittings arising from the methoxy methyl group are smaller than 2 kHz. Therefore, with the resolution of our spectrometer we expect to observe only splittings arising from the ring methyl group. The potential energy curve of the ring methyl group is shown in Figure S-1; the corresponding coefficients in Table S-3 in the Supporting Information.

The microwave spectrum of the only conformer of OMA was then calculated from the *ab initio* predictions with the program XIAM. As a first step, we neglected the internal rotation effect and used the rigid-rotor mode of XIAM to calculate the theoretical spectra. The dipole moment components suggest a spectrum with intense *a*- and *b*-type and no *c*-type transitions. We started our assignment with the *a*-type *R*-branch $J = 6 \leftarrow 5$, especially the transitions $6_{06} \leftarrow 5_{05}$ and $6_{16} \leftarrow 5_{15}$, and then the $J = 5 \leftarrow 4$

transitions such as $5_{05} \leftarrow 4_{04}$. The assignment of these lines fixed the *B* and *C* rotational constants. Afterwards, some *b*-type transitions were also assigned and the *A* rotational constant was determined.

Characteristic patterns of transitions appeared close to those of the *A* species, which were assumed to be the *E* internal rotation symmetry species of the same rotational transitions. In the next step, we took the internal rotation of the ring methyl group into consideration and predicted the spectrum with torsional components using the rotational constants from the rigid rotor fit. The angles δ between the internal rotor axis and the principal *a* axis as well as the V_3 potential were calculated by *ab initio*. In so doing, the *E* species frequencies of many transitions were predicted sufficiently accurate, especially for *a*-type transitions, leading to their straightforward assignment. Finally, we could assign and fit 30 torsional lines in the 10–14 GHz broadband spectrum (shown in Figure 3). Using the prediction refined from this fit, high resolution measurements were performed in the frequency range 2–26.5 GHz, leading to an expanded assignment of 125 *A* and 119 *E* lines and a standard deviation of 2.9 kHz. Figure 4 shows typical transitions of OMA measured at high resolution. The fitted molecular parameters are summarized in Table 1. All fitted transitions are listed in Table S-4 in the Supporting Information.

The three linear combinations of the rotational constants $B_J = \frac{1}{2}(B + C)$, $B_K = A - \frac{1}{2}(B + C)$, $B_- = \frac{1}{2}(B - C)$ and the quartic centrifugal distortion constants were determined with very high accuracy by fitting 244 torsional transitions in a one-rotor fit. The V_3 potential, the angle δ between the internal rotor axis and the principal *a* axis, and two higher order parameters $D_{p_{i2j}}$ and $D_{p_{i2-}}$ were also obtained. The internal rotation constant F_0 of the methyl top could not be fitted because the present data set contains only information on the torsional ground state with relatively low *J* and *K* values, and because the torsional barrier is rather high (459 cm⁻¹).

Table 1. Molecular parameters of *o*-methyl anisole obtained by the program XIAM.

Parameter ^a	Unit	Obs.	Calc. ^b	Obs.–Calc.
<i>A</i>	MHz	2489.335(87)	2481.1078	8.23
<i>B</i>	MHz	1557.68(17)	1558.5760	−0.90
<i>C</i>	MHz	970.516(37)	968.9111	1.60
<i>D_J</i>	kHz	0.03845(63)	0.03655	0.0019
<i>D_{JK}</i>	kHz	0.1583(23)	0.17364	0.0153
<i>D_K</i>	kHz	0.1091(28)	0.03958	0.0695
<i>d₁</i>	kHz	−0.01792(33)	−0.01802	0.0001
<i>d₂</i>	kHz	−0.006296(92)	−0.00668	0.0004
<i>V₃</i>	cm ⁻¹	444.05(41)	459.25	−15.20
<i>F₀</i>	GHz	158.0 ^c	157.9223	0.1
<i>D_{p_{i2j}}</i>	kHz	60.0(7.0)		
<i>D_{p_{i2-}}</i>	kHz	43.6(6.4)		
$\angle(i,a)$	°	70.996(95)	68.8415	2.154
$\angle(i,b)$	°	19.004(95)	21.1586	−2.155
$\angle(i,c)$	°	90.0 ^d	89.970	0.030
<i>N_A/N_E</i> ^e		125/119		
σ^f	kHz		2.9	

^a All parameters refer to the principal axis system. Watson's S reduction and *I* representation were used. ^b Centrifugal distortion constants obtained from anharmonic frequency calculations at the B3LYP/6-311++G(d,p) level of theory, all other values from geometry optimizations at the MP2/6-311++G(d,p) level. ^c Corresponds to $I_a = 3.2$ uÅ², a value often found for methyl groups. ^d Fixed due to C_s symmetry. ^e Number of *A* and *E* species lines. ^f Standard deviation of the fit.

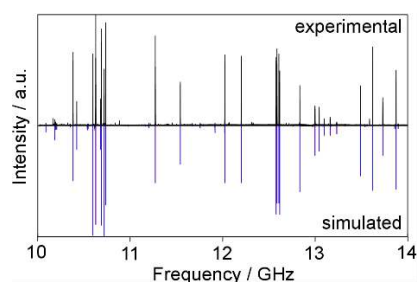


Figure 3. A broadband scan of *o*-methyl anisole from 10 to 14 GHz. The experimental spectrum is the upper trace. The lower trace indicates the theoretical spectrum predicted using the molecular parameters deduced from a one-top fit using the program *XIAM*, showing that (i) a simple one-top model can reasonably reproduce the microwave spectrum of *o*-methyl anisole, and (ii) only some weak lines remained unassigned in the spectrum.

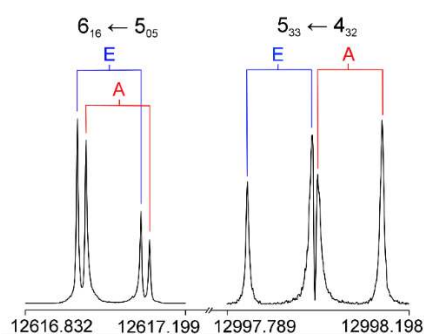


Figure 4. Typical *b*-type and *a*-type transitions (in MHz) of *o*-methyl anisole measured at high resolution. The measurement accuracy is 2 kHz, the typical experimental line width 20 kHz. The doublets marked by brackets are due to the Doppler effect. The torsional A-E splittings are also indicated. For both spectra, 50 free-induction decays were co-added.

The experimentally deduced rotational constants are compared with those from quantum chemical calculations (see Table 1). The experimental and calculated *B* and *C* rotational constants agree well and the deviation in the *A* rotational constant is very small (about 8 MHz). The calculated V_3 potential of 459 cm^{-1} is also quite close to the experimental value of 444 cm^{-1} . The centrifugal distortion constants obtained by anharmonic frequency calculations at the B3LYP/6-311++G(d,p) level of theory are in good agreement with the experimental values. Because the benzene frame of OMA is quite rigid, all centrifugal distortion constants are small. Calculations with the MP2 and B3LYP methods in combination with various basis sets were performed in addition, which confirm that the MP2/6-311++G(d,p) level is sufficiently suitable for OMA, as can be seen in Table S-5 in the Supporting Information. It is noteworthy that the structures obtained from calculations at all levels of theory are consistent, which is not obvious if compared to the case of e.g. diethyl ketone.^[21]

In 2006 Alvarez-Valtierra *et al.* determined the rotational constants $A = 2.4900(1)\text{ GHz}$, $B = 1.5589(1)\text{ GHz}$, and $C = 0.9707(1)\text{ GHz}$ as well as a V_3 potential of 345 cm^{-1} for OMA by fluorescence spectroscopy.^[8] The rotational constants are not as accurate as in the present work, but they are in agreement with those deduced from our fit. On the other hand, the rotational

barrier determined by fluorescence spectroscopy is 99 cm^{-1} lower than our value, which is a significant difference. We believe that the barrier height given by microwave spectroscopy is more reliable, since this parameter was only indirectly determined in fluorescence spectroscopy.

It is interesting to compare the V_3 potential of the ring methyl group in OMA with those of other toluene derivatives, where the substituents are also in the ortho position with respect to each other (see Table 2). In the case of acetates, we found that both the steric and electronic effects might affect the methyl barrier height, where the electronic effect has a larger influence than the steric effect.^[22] In the case of ortho substituted toluene, the influence of the substituent on the barrier height seems to be predominantly of a steric nature. Small or slim substituents such as fluorine atoms (in *o*-fluorotoluene^[23] or 2,4-difluorotoluene^[4]) or cyano groups (*o*-tolunitrile^[24]) hinder the internal rotation much less than voluminous chlorine atoms (*o*-chlorotoluene^[25]), hydroxyl groups (*o*-cresol^[6]), methyl groups (*o*-xylene^[26] or 3,4-dimethylbenzaldehyde^[27]), methoxy groups (OMA), or aldehyde groups (2,5-dimethylbenzaldehyde^[27]). In molecules where *syn*- and *anti*-conformers co-exist in the spectrum, the *anti*-conformer has lower internal rotation barrier, because the ortho substituent is much closer to the methyl group, and the steric hindering increases, while the electronic contribution should be similar for both conformers. An electronic effect is, however, not excluded, as can be seen from the different V_3 potential of *o*-fluorotoluene^[23] and 2,4-difluorotoluene^[4] or *o*-xylene^[26] and 3,4-dimethylbenzaldehyde.^[27] Nevertheless, these differences are less significant.

The planar moment of inertia $P_{cc} = -2(l_c - l_a - l_b) = 13.396\text{ u}\text{\AA}^2$ of OMA confirms that the heavy atom skeleton is planar with two pairs of hydrogen atoms out of plane. These values are very similar as that found in other planar molecules containing two methyl groups such as the *trans* and *cis* conformers of 2-acetyl-5-methylfuran ($P_{cc} = 12.938$ and $13.160\text{ u}\text{\AA}^2$, respectively)^[18] and the *syn* and *anti* conformers of 3,4-dimethylbenzaldehyde ($P_{cc} = 12.904$ and $12.938\text{ u}\text{\AA}^2$, respectively).^[27]

After the spectral assignment, only very few weak lines remained unassigned in the broadband scan, as shown in Figure 3. We thus concluded that water complexes or dimers were not present under our measurement conditions.

Table 2. Torsional barriers of ortho substituted toluene derivatives.

	V_3/cm^{-1}	Ref.
<i>o</i> -tolunitrile	187.699(3)	[24]
<i>o</i> -fluorotoluene	227.28(2)	[23]
2,4-difluorotoluene	203.91(24)	[4]
<i>anti</i> - <i>o</i> -cresol	371.05(41)	[6]
<i>syn</i> - <i>o</i> -cresol	669.10(51)	[6]
<i>o</i> -methyl anisole	444.05(41)	this work
<i>anti</i> -3,4-dimethylbenzaldehyde	454.1(14), 480.6(44)	[27]
<i>syn</i> -3,4-dimethylbenzaldehyde	508.1(11), 550.7(88)	[27]
³⁷ Cl- <i>o</i> -chlorotoluene	507.2(83)	[25]
³⁵ Cl- <i>o</i> -chlorotoluene	513.8(27)	[25]
<i>o</i> -xylene	518.3(32)	[26]
<i>syn</i> -2,5-dimethylbenzaldehyde	566(16)	[27]

Experimental section

A broadband scan from 10 to 14 GHz was recorded, where overlapping spectra with a step width of 250 kHz and 50 co-added free-induction decays were automatically taken using a molecular jet Fourier-transform microwave spectrometer operating in the frequency range from 2 to 26.5 GHz.^[28] OMA was purchased from TCI Europe, Eschborn, Germany, with a stated purity of 98 %. Without any further purification, the substance was placed on a 5 cm piece of a pipe cleaner inside a stainless steel tube mounted upstream the nozzle because of its low vapor pressure. Under helium stream at a backing pressure of 200 kPa, the OMA-He mixture was expanded into the cavity. All lines in the broadband scan (Figure 3) were subsequently remeasured at higher resolution with an intrinsic experimental line width of 2 kHz for isolated lines,^[29] indicating completely resolved torsional splittings due to internal rotation of the ring methyl group (Figure 4). The average value of the line widths is about 20 kHz, corresponding to a measurement accuracy of 2 kHz. The line broadening was probably due to unresolved proton hyperfine splittings or unresolved splittings arising from the internal rotation of the methoxy methyl group. All rotational signals appeared in addition to the torsional splittings as doublets due to the Doppler effect. The molecular transition frequency is the center frequency of these doublets.

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Keywords: structure determination • microwave spectroscopy • internal rotation • rotational spectroscopy

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COMMUNICATION

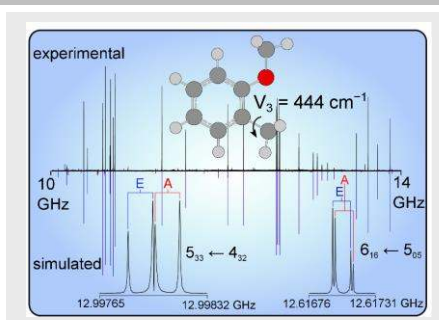
Entry for the Table of Contents (Please choose one layout)

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COMMUNICATION

Rotating on the ring – the methyl torsional barrier

Torsional splittings due to the internal rotation of the ring methyl group of *o*-methyl anisole were analyzed by microwave spectroscopy. The barrier to internal rotation was accurately determined. Results from quantum chemistry are in agreement with the experiments.



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Methyl Internal Rotation in the Microwave Spectrum of *o*-Methyl Anisole