Microwave and theoretical investigation of the internal rotation in *m*-cresol

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The microwave spectrum of *m*-cresol (3-methylphenol) has been investigated using a molecular beam Fourier transform microwave spectrometer in the frequency range from 3 to 26.5 GHz. The rotation of the hydroxy group into two different unequal energetic minima leads to different spectra for the syn- and anticonformers. Because of a high potential barrier both conformers can be analyzed independently. The methyl group is undergoing an almost free internal rotation which is only hindered by small barriers and splits the vibrational ground state in two states of internal rotation denoted as A and E species. The spacing between the species is found to be up to 10 GHz. The potential for the internal rotation can be determined from the spectra and analyzed in terms of the Fourier components V_3 and V_6. For syn-*m*-cresol these parameters were determined as $V_3=673(3)$ GHz and $V_6=-335(24)$ GHz and for anti-*m*-cresol $V_3=95(5)$ GHz and $V_6=-416(46)$ GHz. The barriers to internal rotation were furthermore calculated with second-order Møller-Plesset perturbation theory and second-order coupled-cluster singles- and-doubles model (CC2) in the electronic ground state and with CC2 in the first excited state. The CC2 method is found to be an appropriate method to calculate potential barriers in electronic excited states of such compounds. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2198842]

I. INTRODUCTION

Internal rotation in molecules has been a subject of investigations since Kemp and Pitzer[1] concluded on 1936, from calorimetric measurements, that the rotation of the methyl groups in ethane is hindered by a potential barrier. A quantum mechanical treatment for the torsion oscillator rotator has been given four years earlier by Nielsen.[2] The barrier and its origin for this very molecule are still being discussed nowadays, see, for example, Refs. 3 and 4 and references therein. Torsional potentials are responsible for the conformation of molecules and intramolecular motions. The possibility of computing these potentials with sufficient accuracy is not only important for the understanding of molecular spectra, but is also interesting for the engineering of molecular functionality. Today microwave spectroscopy is the most accurate method to determine the potential barriers to internal rotation.[5,6] The theoretical formalism for treating the internal rotation of a symmetrical top on an asymmetrical frame is well established for a long time and many internal motions have been resolved by means of it.[7,8] Yet studies on molecules with low barriers to internal rotation often experience difficulties to reproduce the experimental data sufficiently with model parameters.[9–12] Bruhn and Mäder[10] overcame these problems by use of an additional torsional state-dependent centrifugal distortion term in the Hamiltonian plus a robust fitting procedure. Subramanian *et al.*[12] used also an additional nonstandard term for their fit described as a higher-order torsion-rotation coupling term. In the present work we analyzed the experimental transitions by using different sets of rotational constants for the A and E species and we included besides the Fourier coefficient V_3 also the V_6 term, which is highly correlated to V_3 but nevertheless improves the fit and, as shown later, is in good agreement with *ab initio* calculated values.

The internal rotation in substituted toluenes has been investigated with quantum chemical programs since 1995.[13,14] Most of these studies are done with Hartree-Fock (HF), density functional (DFT), or second-order Møller-Plesset perturbation theory (MP2). To our knowledge no coupled-cluster method has yet been applied to this kind of problems. With MP2 calculations it is possible to obtain torsional potentials that are in good agreement with the experimental values (see, for example, Refs. 10 and 15–17) for electronic ground states. Only a few studies deal with the internal rotation in excited states for such systems. Toluene and its methyl mono- and dideuterated isotopomers have been investigated with complete-active space self-consistent field (CASSCF) theory in S_0 and S_1.[18] The barrier to internal rotation in substituted toluenes has been calculated in the first electronic excited state S_1 with configuration interaction with single excitations (CIS).[19]

The second-order coupled-cluster singles-and-doubles model (CC2) (Ref. 20) was developed as an approximation to the CCSD method. CC2 yields for the ground state results within a similar accuracy as MP2 and scales with the system size as MP2 with $O(N^5)$, but in contrast to MP2 it is applicable to response theory and can be used to study also ex-

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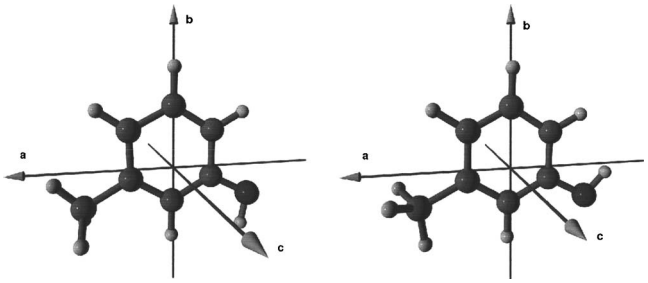


FIG. 1. The syn- and anticonformers of *m*-cresol.

cited states. Both methods can be implemented very efficiently using the resolution of the identity (RI) approximation.[21,22] This makes CC2 an ideal candidate for *ab initio* calculations of torsional potentials in excited states at reasonable computational costs.

The present communication is the second paper in a series of microwave studies on cresols. The results of an investigation of *o*-cresol[16] have been published recently and a manuscript on *p*-cresol is in preparation. *m*-Cresol along with the other two cresols has earlier been investigated theoretically by Kudchadker *et al.*[23] using the semiempirical CNDO/2 method. The energies of the syn- and anticonformers (see Fig. 1 for a sketch) were calculated in the staggered and the eclipsed position of the methyl group. The anticonformer in the staggered position was found to be the most stable configuration. From the relative energy differences the barrier heights were proposed. Nakai and Kawai[19] calculated the potential curves of the methyl rotation in *m*-cresol among with other substituted toluenes at the HF level in the ground state (S_0) and with CIS in the first electronic excited state (S_1).

Mizuno *et al.*[24] studied the fluorescence excitation, dispersed fluorescence, and two-color ionization threshold spectra of *m*-cresol. High resolution investigations with laser induced fluorescence spectroscopy on cresols and cresol/water clusters were reported by Schmitt[25] and recently by Myszkiewicz *et al.*[26] The latter yielded accurate data for the barrier heights in S_0 and S_1.

II. THEORY

The spectra recorded in the scope of this work all belong to the vibrational ground state $\nu=0$ which is split into two symmetry species denoted as A and E species. These species are equivalent to the states described by the free rotor quantum numbers $m=0$ and $m=\pm 1$, respectively. The microwave transitions have been analyzed using the rotation-torsion Hamiltonian,[5]

$$\hat{H} = \hat{H}_{\mathrm{rot},\Gamma} + \hat{H}_{\mathrm{cd}} + \hat{H}_{\mathrm{ir}} \quad \text{with } \Gamma \in \{A,E\}. \tag{1}$$

For the rotational contribution of the Hamiltonian separate sets of rotational constants A_Γ, B_Γ, and C_Γ were chosen to account for the two symmetry species.

$$\hat{H}_{\mathrm{rot},\Gamma} = A_\Gamma \hat{J}_a^2 + B_\Gamma \hat{J}_b^2 + C_\Gamma \hat{J}_c^2. \tag{2}$$

With this approach different couplings between vibrations and rotation or vibrations and torsion in the A and E state can be compensated. It also takes structural deformations induced by the methyl torsion into account. Therefore these rotational constants are contaminated by other interactions and have to be considered as effective parameters. Nevertheless in this framework the rotational constants for the A species will surely be close to the structural rotational constants, because the transitions of the E species are the ones that actually trouble the analysis of the data.

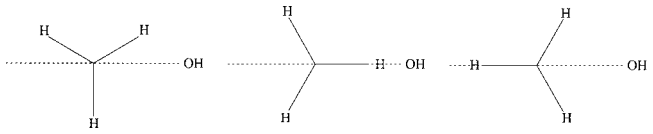


FIG. 2. The characteristic positions of the methyl group with respect to the hydroxy group are called (from left to right) perpendicular, eclipsed, and staggered.

The centrifugal distortion part contains the fourth order terms of the components $\hat{J}_g$, $g \in \{a,b,c\}$ of the angular momentum operator $\hat{J}$ using Watson's A reduction[27] in the I^r representation.

$$\hat{H}_{\mathrm{cd}} = -\Delta_J \hat{J}^4 - \Delta_{JK} \hat{J}^2 \hat{J}_a^2 - \Delta_K \hat{J}_a^4 - 2\delta_J \hat{J}^2 (\hat{J}_b^2 - \hat{J}_c^2) - \delta_K [\hat{J}_a^2 (\hat{J}_b^2 - \hat{J}_c^2) + (\hat{J}_b^2 - \hat{J}_c^2)\hat{J}_a^2]. \tag{3}$$

The Hamiltonian for the internal rotation and the coupling of internal rotation to overall rotation is given by[7,8]

$$\hat{H}_{\mathrm{ir}} = F(\hat{j}_\alpha - \rho_\alpha \hat{J}_a - \rho_b \hat{J}_b)^2 + V(\alpha). \tag{4}$$

The first term describes the kinetic energy, where F is the reduced rotational constant for the methyl top and $\rho_g = \lambda_g I_\alpha / I_g$, with I_α the moment of inertia of the top, I_g the moments of inertia of the molecule, and λ_g the direction cosine between the internal rotor axis and the principal axis g for $g \in \{a,b\}$.

The potential for the internal rotation, which has a local three-folded symmetry axis, can be approximated as

$$V(\alpha) = \frac{V_3}{2}(1 - \cos 3\alpha) + \frac{V_6}{2}(1 - \cos 6\alpha), \tag{5}$$

where α is the torsional angle of the methyl group relative to the molecular frame.

The data analysis was performed with the program XIAM (Ref. 28) employing the combined axis method.

During a full rotation the methyl group has three characteristic positions shown in Fig. 2. The position denoted as perpendicular stabilizes via hyperconjugation and is the energetic favored position. This will not be recognized on the HF level. To obtain reliable *ab initio* results for the potential parameters V_3 and V_6 in substituted toluenes electron correlation effects have to be taken into account. MP2 gives ground state and CC2 ground and singly excited state energies correct through second order in the fluctuation potential of the electronic part of the molecular Hamiltonian,

$$H_{\mathrm{el}} = f + U, \tag{6}$$

where f is the Fock matrix, and U is the fluctuation potential.

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TABLE I. The calculated dipole moments of *m*-cresol in debye units.

	MP2/TZVPP	MP2/QZVPP	CC2/TZVPP	CC2/QZVPP
Syn-*m*-cresol				
μ_a	1.02	1.06	0.97	1.02
μ_b	−1.23	−1.22	−1.26	−1.24
$\|\mu\|$	1.60	1.62	1.59	1.61
Anti-*m*-cresol				
μ_a	−0.32	−0.26	−0.35	−0.29
μ_b	0.96	0.96	0.92	0.92
$\|\mu\|$	1.01	1.00	0.99	0.97

III. EXPERIMENTAL DETAILS

m-Cresol was purchased from Lancaster Synthesis GmbH, Mühlheim/Main, Germany (>99%) and was used without further purification. The measurements were carried out with a pulsed nozzle molecular beam Fourier transform microwave (MB-FTMW) spectrometer covering the frequency range from 3 to 26.5 GHz. The spectrometer design is similar to that described by Balle and Flygare.[29] The specific setup has been described in Ref. 30. The molecular beam is introduced along the cavity symmetry axis.[31] A resolution better than 1 kHz is hereby archived.

Due to the fact that *m*-cresol has a boiling point of 203 °C and a very low vapor pressure, the substance was kept in a stainless steel vessel in front of the nozzle, was heated up to about 30–60 °C and expanded to the vacuum tank in a stream of rare gas. Helium at a stagnation pressure of 1–2 bars was used as carrier gas. Thereby a gas mixture containing about 1% *m*-cresol was produced. Through the adiabatic expansion and collisions with the carrier gas the supersonic jet acquires a temperature of about 4 K. The syn-*m*-cresol showed an equally strong *a*- and *b*-type spectra, while in the spectrum of anti-*m*-cresol the *a*-type transitions were found to be very weak. This can be explained by the different dipole moments in the two conformations. The results of the MP2 and CC2 calculations (Table I) show that the dipole moment along the principle axis *a* in anti-*m*-cresol is considerably smaller than the other. The measured transitions and their observed-to-calculated differences are given in the supplementary material (Tables S1 and S2).[32]

TABLE II. Comparison of potential coefficients of internal rotation in the ground state given in cm^{-1}

	Syn		Anti	
	V_3	V_6	V_3	V_6
Experimental				
This work	22.44(7)	−11.2(8)	3.2(2)	−13(2)
Mizuno *et al.*[a]	26	−9	11	−8
Schmitt *et al.*[b]	21.34(5)	⋯	3.2(2)	⋯
Calculations				
CNDO/2[c]	28.7	⋯	5.6	⋯
HF/6-31G**[d]	37	⋯	12	⋯
MP2/TZVPP	25.0	−14.9	3.5	−14.4
MP2/QZVPP	23.2	−11.0	3.6	−10.3
CC2/TZVPP	24.3	−15.2	1.6	−15.1
CC2/QZVPP	22.6	−10.8	1.5	−10.1

[a]Reference 24.
[b]Reference 26.
[c]Reference 23.
[d]Reference 19.

TABLE III. Comparison of potential coefficients of internal rotation in the first electronically excited state S_1 given in cm^{-1}.

	Syn		Anti	
	V_3	V_6	V_3	V_6
Experimental				
Mizuno *et al.*[a]	211	−39	213	−22
Schmitt *et al.*[b]	221.8(3)	−29.8(2)	204.3(5)	−28.4(3)
Calculations				
CIS/6-31G**[c]	268	⋯	241	⋯
CC2/TZVPP	265.3	−54.1	272.5	−36.9
CC2/QZVPP	278.1	−33.1	276.9	−28.2

[a]Reference 24.
[b]Reference 26.
[c]Reference 19.

IV. COMPUTATIONAL METHODS

We have carried out a series of *ab initio* calculations for the ground state and the first electronically excited state with the RICC2 program[22] which is part of the TURBOMOLE package.[33] The polarized triple- and quadruple-ζ basis sets TZVPP (Ref. 34) and QZVPP (Ref. 35) were used together with the respective optimized auxiliary basis sets reported in Refs. 36 and 37.

For the calculation of the potential for the internal rotation we varied the torsional angle of the methyl group between 0° (eclipsed) to 60° (staggered) in steps of 10°, while all remaining coordinates were fully optimized. In the eclipsed position one hydrogen atom is synperiplanar with the hydroxy group, while in the staggered position two hydrogen atoms take positions most distant from the hydroxy group (see Fig. 2). The potential of the staggered structure is arbitrarily set to zero except for the ground state S_0 of the

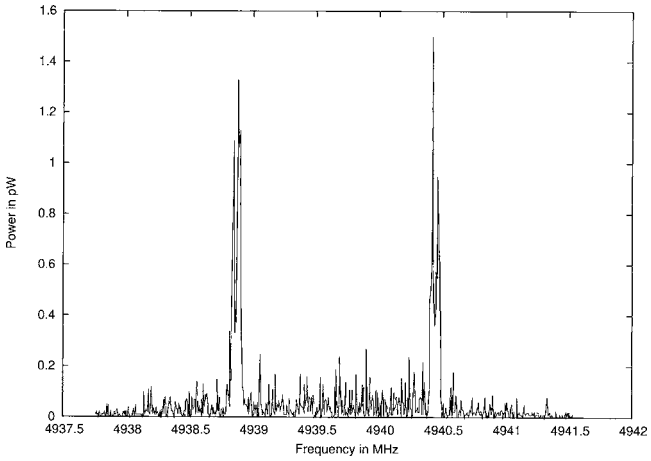


FIG. 3. The power spectrum of the $1_{11}-0_{00}$ transition at a temperature of 30 °C in the reservoir in front of the nozzle.

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TABLE IV. The differences of the calculated rotational constants and the observed ones of the A species for *m*-cresol in GHz.

	MP2/TZVPP	MP2/QZVPP	CC2/TZVPP	CC2/QZVPP
Syn-*m*-cresol				
ΔA	0.014 705	0.025 175	0.005 703	0.015 982
ΔB	0.005 547	0.010 812	0.002 098	0.007 216
ΔC	0.004 075	0.007 607	0.001 517	0.004 965
Anti-*m*-cresol				
ΔA	0.012 485	0.022 974	0.003 224	0.013 476
ΔB	0.006 204	0.011 480	0.002 892	0.008 047
ΔC	0.004 148	0.007 690	0.001 628	0.005 093

anticonformer, for which the eclipsed structure is lower in energy and thus used as reference point. With this procedure the torsional potentials for the equilibrium structures were emulated. The constants V_3 and V_6 in the potential function (5) were determined by a least squares fit. The results are given in Table II for the ground state and Table III for the first excited state.

In the equilibrium structures the hydroxyl group is for both conformers coplanar with the benzene ring, and the methyl group is oriented perpendicular to it with a torsional angle of about 30°.

V. RESULTS AND ANALYSIS

The syn- and anticonformers appear in the spectra like two different species and were thus assigned and analyzed independently of each other. A way to distinguish one conformer experimentally from the other is to record the same transition at different mixture of the conformers. Figures 3 and 4 are spectra that contain a transition from each of the conformers. Both spectra were recorded at the same conditions except for the temperature in the reservoir in front of the nozzle. This temperature is used to regulate the ratio of the syn/anticonformers outside of the vacuum tank. When the pulsed molecular beams are produced, a rotational temperature in the beam of about 4 K is achieved (see Sec. III), the torsion of the hydroxyl group is thereby frozen out and the ratio of the mixture will stay unchanged.

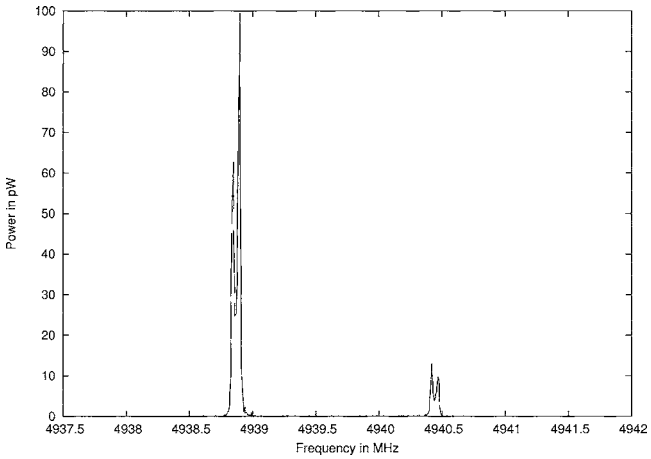


FIG. 4. The power spectrum of the $1_{11}-0_{00}$ transition at a temperature of 61 °C in the reservoir in front of the nozzle.

It is the $1_{11}-0_{00}$ transition of the syn and anticonformers. The transitions are split in two signals due to the Doppler effect. Although the signal-to-noise ratio is not very good at 30 °C, the ratio of the signals clearly changes with the temperature, with the relative intensity of the signal at lower

TABLE V. Molecular parameters of *m*-cresol in Watson's A reduction.

		Syn		Anti	
Parameter		A	E	A	E
A	(GHz)	3.666025(8)	3.66576(2)	3.66135(2)	3.66240(8)
B	(GHz)	1.7933582(5)	1.793632(2)	1.797153(1)	1.797218(8)
C	(GHz)	1.2133803(1)	1.21342670(1)	1.2145872(2)	1.2145818(5)
D_J	(kHz)	0.070(1)	0.070(1)	0.069(2)	0.069(2)
D_{JK}	(kHz)	−0.119(6)	−0.119(6)	−0.054(6)	−0.054(6)
D_K	(kHz)	1.06(2)	1.06(2)	0.74(1)	0.74(1)
d_j	(kHz)	0.0235(6)	0.0235(6)	0.0250(7)	0.0250(7)
d_k	(kHz)	0.079(8)	0.079(8)	0.134(8)	0.134(8)
V_3	(GHz)	672(2)	672(2)	94(5)	94(5)
V_3	(cm^{-1})	22.44(7)	22.44(7)	3.2(2)	3.2(2)
V_6	(GHz)	−335(24)	−335(24)	−416(46)	−416(46)
V_6	(cm^{-1})	−11.2(8)	−11.2(8)	−13(2)	−13(2)
I_α	(amu Å^2)	3.131[a]	3.131[a]	3.132[a]	3.132[a]
$\angle(\alpha,a)$[b]	(deg)	28.9985(4)	28.9985(4)	29.188(1)	29.188(1)
$\angle(\alpha,b)$[b]	(deg)	118.9985(4)	118.9985(4)	119.188(1)	119.188(1)
$\angle(\alpha,c)$[b]	(deg)	90.0[a]	90.0[a]	90.0[a]	90.0[a]
σ[c]	(kHz)	4.0	4.0	9.6	9.6
N[d]		124	33	147	18

[a]Fixed to *ab initio* value.
[b]Angle between the internal rotor axis and the principle axis.
[c]Standard deviation.
[d]Number of transitions.

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TABLE VI. The angle in deg between the internal rotor axis α and the principal axis a from *ab initio* calculations.

	MP2/TZVPP	MP2/QZVPP	CC2/TZVPP	CC2/QZVPP
Syn	29.46	29.42	29.47	29.46
Anti	29.47	29.42	29.47	29.43

frequency increasing with the temperature. This indicates that the transition with the higher frequency belongs to the more stable conformer. A ground state calculation with CC2/QZVPP at equilibrium geometries yielded that the anticonformer has a total energy which is 0.1 kJ/mol lower than the one of the synconformer. With this result and the comparison of the rotational constants in Table IV, the conformers can be assigned. Thus the transitions at the lower frequency belong to the synconformer and the other to the anticonformer.

The A/E splitting is rather large (up to 10 GHz) and made it necessary to do the assignment step by step. While it was straightforward for the A species, where the spectra match the pattern of a distorted asymmetrical rotor, the assignment for the E species was more involved because of stronger perturbations in the spectra.

Restricted least square fits of the molecular parameters defined in Sec. II to the observed transitions lead to the values given in Table V.

The moment of inertia of the top I_α could not be deduced from the spectra, since it has little influence on the transitions. While first fits were done with an educated guess for I_α of 3.159 amu Å^2, the final results were obtained with I_α fixed to the results of the CC2/TZVPP calculations. The fact that the Fourier parameters V_3 and V_6 are in the same order of magnitude can be explained with the symmetry of the molecule. It has a global C_{3v} symmetry, but in the area of the rotor axis a local C_{6v} symmetry. The algebraic sign of V_6 could not be revealed from the analysis of the spectra. It was set to minus following results of the calculations.

In Table IV are the differences between the calculated and the observed rotational constants listed. (The calculated equilibrium structures are given in the supplementary material,[32] Tables S3 and S4). Since the structural rotational constants are put together from the positions of all the atoms of the r_0 structure the difference to the calculated r_e structure can sum up. For this reason rotational constants are not good values for a comparison of experiments and calculations. Such a comparison is more meaningful for a single atomic bond or an internal angle. In Table VI the calculated angles between the internal rotor axis α and the principal axis a are shown. The values differ less then 0.5° from the experimental values.

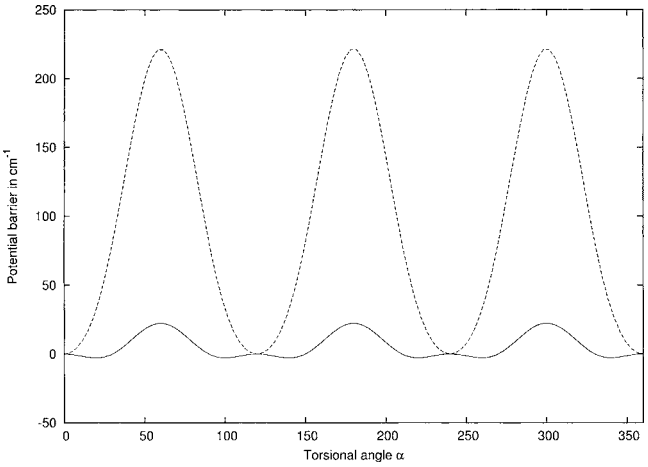


FIG. 5. The potential curves in S_0 (solid line) and S_1 (dotted line) of the synconformer from the experimental values of this work and Ref. 26.

The comparison in Table II of V_3 in the ground state shows that the experimental values are consistent with data from Ref. 26. The value of V_6 are quite close to results from the low resolution spectra in Ref. 24. The accuracy of the MP2 and CC2 calculations is much higher than that of prior theoretical investigations at CNDO/2 and HF levels, and thus the present results are more reliable. Also both, MP2 and CC2, yield nearly the same results for the electronic ground state. The step from the TZVPP basis set to QZVPP is in this case the step into the borders of the experimental uncertainty.

The barrier height increases by a factor of about 10 in the first excited state. The results of the calculations in the S_1 state are given in Table III. To illustrate the situation the potential curves of S_0 and S_1 are plotted in Fig. 5 for the synconformer. In the ground state V_3 and V_6 are of the same order of magnitude. From this it follows that the potential curve has not only three global maxima during a full rotation of the methyl group, but also three local maxima. In the first electronically excited state V_3 is by an order of magnitude larger than V_6. Thus, the potential has only three extrema, just the slopes are affected by V_6.

The most conspicuous structural changes upon electronic excitation are the increase of the CC ring bonds, on average 0.3 Å, and a shortening of the CO bond and the CC bond between the ring and the methyl group.

Although the TZVPP basis set yields results that are in good agreement with the experiment, it can be seen in Table III that the ratio of the barriers of the two conformers changes when applying a higher basis set. With the TZVPP basis set V_3 for the anticonformer seems to be higher than for the synconformer. With QZVPP this situation is turned around. The differences between the conformers are quite small, but nevertheless the results agree with the recent experiment.[26]

VI. CONCLUSIONS

We have measured the rotational spectra of syn- and anti-*m*-cresol in the two lowest states of internal methyl rotation. It was found to be necessary to use two sets of rotational constants for the A and E species and to include the Fourier parameter V_6 in the fitting routine to reproduce the experimental spectra decently. The internal rotation analysis yielded parameters for the internal rotation which are in good agreement with *ab initio* results.

The drastic change of the barrier height from S_0 to S_1 has been noticed in many molecules with a methyl rotor attached to an aromatic ring (see Refs. 38 and references therein for examples). With the RI-CC2 approach it is possible to obtain results with spectroscopic accuracy for such systems.

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