The smell of coffee: the carbon atom microwave structure of coffee furanone validated by quantum chemistry

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ABSTRACT

The rotational spectra of coffee furanone (2-methyltetrahydrofuran-3-one) have been measured in the frequency range from 2.0 to 26.5 GHz using a molecular jet Fourier transform microwave spectrometer. Quantum chemical calculations used for the conformational analysis yielded two stable *twist* conformers, which were described using the Cremer-Pople notation for five-membered rings. The experimental spectrum of the more stable conformer with the methyl group in *equatorial* position was assigned and fitted using a rigid rotor model with centrifugal distortion corrections. The spectra of all five ^{13}C-isotopologues could be observed in natural abundance. The carbon atom structure was experimentally deduced using Kraitchman's equations and compared with the structure calculated by quantum chemistry.

TOC GRAPHICS
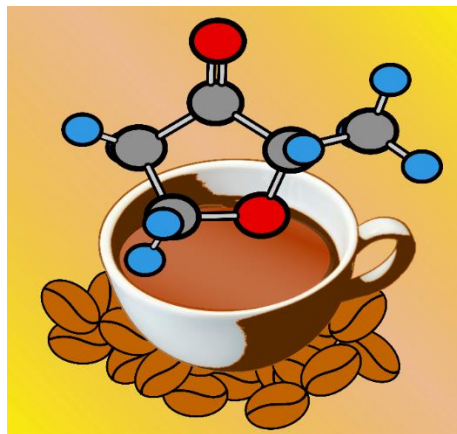
KEYWORDS

Rotational spectroscopy, conformational analysis, structure determination, five-membered ring.

1. Introduction

Coffee is a very popular drink in the daily life of millions of people in many countries as a first hot beverage in the morning. Several methods have been investigated and created to produce this drink including different extraction techniques and roasting processes. The coffee aroma is quite complex with more than 800 identified volatile compounds.[1] Since the bean roasting and the brewing of coffee each has many process parameters to create the desired aroma, deep knowledge about the composition of the volatile aroma is necessary.[2,3] One of these compounds is the five-membered heterocyclic molecule 2-methyltetrahydrofuran-3-one, popularly known as coffee furanone, which is also a natural flavor in tomatoes[4] and pork.[5] In addition, it was identified in the Maillard reaction which is responsible for the creation of important roasting aromas when food is browned.[6]

In the present study we investigate the microwave spectrum from a supersonic expansion to understand the gas phase structure of this important coffee aroma compound. The experimental work is supported by quantum chemical calculations, where *ab initio* structures are taken as references for a comparison of the experimental and calculated molecular parameters.

2. Quantum chemical calculations

Coffee furanone features an ether group in the ring as well as a carbonyl group and a methyl group as substituents (see Figure 1). To sample the conformational landscape of coffee furanone, the two conformers of cyclopentane twist (C_2) and bent (C_s)[7] were used and modified to generate the starting geometries. Two CH_2 units were exchanged by a carbonyl group and an oxygen atom, and a methyl group was added in between at either equatorial or axial position. The modified structures

were subsequently optimized at the MP2/6-311++G(d,p) level of theory using the *GAUSSIAN09* program suite.[8] From our experiences on other five-membered rings, the MP2/6-311++G(d,p) level yielded rotational constants close to the experimental values to start the spectral assignment.[9,10]
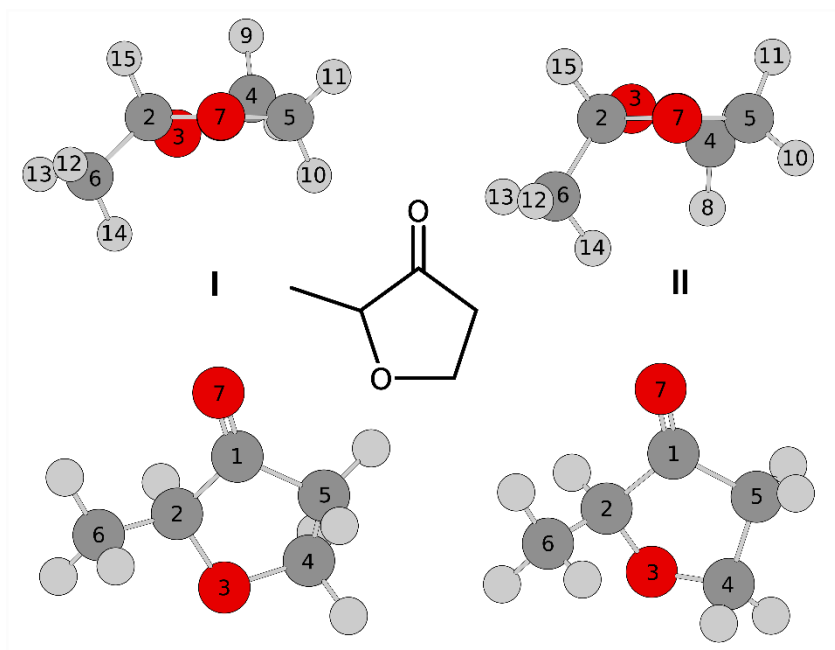
Figure 1. The structures of conformer I (left hand side) and II (right hand side) calculated at the MP2/6-311++G(d,p) level as well as the structural formula of coffee furanone (middle figure). Upper figures: view along the carbonyl bond C_1–O_7. Lower figures: view onto the furan ring. The energy difference between conformer II and the more stable conformer I is 4.34 kJ·mol^{-1}. The carbon atom C(1) is located behind the oxygen atom O(7).

The geometry optimizations yielded two *twist* conformers (I and II) as shown in Figure 1. Conformer I with the rotational constants $A = 3530$ MHz, $B = 3119$ MHz, and $C = 1802$ MHz is 4.34 kJ·mol^{-1} lower in energy than conformer II ($A = 3486$ MHz, $B = 3116$ MHz, and $C = 1921$

MHz). Harmonic frequency calculations at the same level of theory confirmed that they are true minima. Furthermore, various combinations with the HF, B3LYP, MP2, M06-2X, and CCSD methods and different basis sets were used to re-optimize the structures of conformer I and II to check for convergence. The Cartesian coordinates are given in Table S-1; the rotational constants are in Table S-2 in the Supporting Information.

The ring geometries of both conformers can be characterized using the Cremer-Pople puckering parameters[11] calculated with the program *RING*[12] to characterize the ring geometries. There are two parameters for a five-membered ring, the phase angle ϕ_2 and the puckering amplitude q_2.[11] The calculated geometry of conformer I has the *twist* structure ${}^3T_4$ and the methyl substituent is in inclined orientation with $q_2 = 0.38$ and $\phi_2 = 92.3$. Conformer II also has a *twist* structure ${}^4T_3$ with a little more envelope contribution of the *envelope* structure ${}^4E$ and the methyl substituent in *axial* orientation with $q_2 = 0.35$ and $\phi_2 = 277.6°$. The optimized conformers of coffee furanone and some other related five-membered rings studied in the literature[13-16] are illustrated in Figure 2 using the Cremer-Pople coordinates and the model of Altona and Sundaralingam.[17]
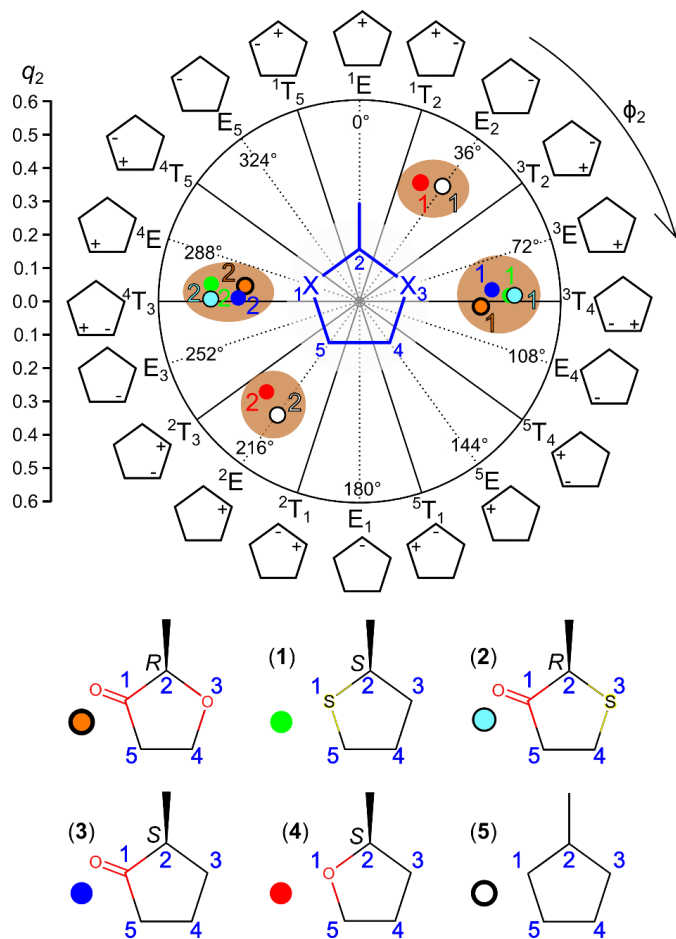
Figure 2. Conformational landscape of coffee furanone (orange dots) and related five-membered rings using two Cremer-Pople parameters q_2 (puckering amplitude) and ϕ_2 (phase angle). The nomenclature is based on the **T**$wist$ or **E**$nvelope$ geometry and the positions of the atoms which are above (+) and below (−) the ring plane. A planar ring would be located at the center with $q_2 = 0$. Upper figure: 1 and 2 represent the two conformers of each molecule. Lower figure: (**1**) 2-Methyltetrahydrothiophene (green dots), (**2**) dihydro-2-methyl-3-thiophenone (cyan dots), (**3**) 2-methylcyclopentanone (blue dots), (**4**) 2-methyltetrahydrofuran (red dots), and (**5**) methylcyclopentane (white dots).

3. Microwave spectroscopy

Coffee furanone was purchased from TCI Europe, Zwijndrecht, Belgium, with a stated purity of 98 % and used without further purification. The rotational spectra were measured with a molecular jet Fourier transform microwave (FTMW) spectrometer operating in the frequency range 2 – 26.5 GHz.[18] The substance was placed on a piece of a pipe cleaner close to the nozzle under a helium stream at a pressure of approximately 200 kPa. For an overview of the rotational spectra, a survey sprectrum was recorded in the frequency range from 9 to 14 GHz, where overlapping spectra are automatically recorded at a step width of 0.25 MHz with 50 co-added decays per spectrum. Transitions appearing in the scan were subsequently remeasured at higher resolution, where all lines appear as doublets due to the Doppler effect. The line widths range from 12 to 33 kHz, which correspond to a measurement accuracy of about 2 kHz.

We started the spectral assignment with the most stable conformer I. Because the predicted values of the dipole moment components are $|\mu_a| = 2.25$ D, $|\mu_b| = 0.62$ D, and $|\mu_c| = 0.34$ D, we expected strong a-type, medium b-type, and weaker c-type transitions. At the beginning, the a-type R-branch $3_{03} \leftarrow 2_{02}$ and $3_{13} \leftarrow 2_{12}$, as well as two b-type R-branch transitions $3_{03} \leftarrow 2_{12}$ and $3_{13} \leftarrow 2_{02}$ were considered. As these four transitions form a closed loop, they could be identified straightforward and all rotational constants were determined. This allowed us to measure further lines up to $J = 10$ (including c-type transitions) within the frequency range of the spectrometer and to fit all five quartic centrifugal distortion constants. In total, 122 transitions were assigned and fitted with a program written by the authors for Separately Fitting Large Amplitude Motion Species (*SFLAMS*) to a root mean square (rms) deviation of 2.6 kHz. Coffee furanone can be treated as a rigid rotor, fitting the large amplitude motion torsional symmetry species A with the Hamiltonian only comprising the rotational terms with quartic centrifugal distortion corrections

using Watson's S reduction. All fitted molecular parameters are summarized in Table 1. The frequency list is given in Table S-3 in the Supporting Information.

The most intense lines in the survey spectrum clearly belong to conformer I. However, about half of the lines with much weaker intensity remain unassigned in the spectrum (see Figure 3). All attempts to assign these lines to conformer II failed. As mentioned, conformer II is 4.34 kJ·mol^{-1} higher in energy than conformer I. In our investigations on two other five-membered rings, 2-methyltetrahydrothiophene[13] and dihydro-2-methyl-3-thiophenone,[14] which possess two similar *twist* structures with smaller energy difference, the assignment of the less stable conformer was straightforward. Therefore, we believe that conformer II of coffee furanone is not present under our molecular jet conditions with a very low rotational temperature of less than 2 K.

Table 1. Experimentally deduced molecular parameters of the parent species and the different isotopologues of conformer I of coffee furanone using the program *SFLAMS*. The parameters of the parent species (denoted as ^{12}C) are compared with the vibrational ground state values A_0, B_0, and C_0 calculated by anharmonic frequency calculation at the MP2/6-311++G(d,p) level of theory. For all isotopologues, the atoms are numbered according to Figure 1.

Par.[a]	Unit	^{12}C	MP2	$^{13}C(1)$	$^{13}C(2)$	$^{13}C(4)$	$^{13}C(5)$	$^{13}C(6)$
A	MHz	3539.55633(14)	3500.8	3522.7879(17)	3525.7174(17)	3537.9674(21)	3511.18487(47)	3501.0819(21)
B	MHz	3111.02316(13)	3093.8	3109.04417(78)	3104.17775(83)	3051.17018(85)	3083.45810(48)	3054.93511(87)
C	MHz	1796.24912(13)	1786.5	1791.30837(40)	1792.32059(37)	1775.89332(38)	1780.90831(25)	1768.45796(45)
D_J	kHz	0.2591(26)	0.2113	0.212(31)	0.208(32)	0.215(33)	0.355(81)	0.213(34)
D_{JK}	kHz	−0.0544(24)	0.4977					
D_K	kHz	1.2628(28)	0.5222	1.51(40)	1.63(41)	1.41(48)		1.54(47)
d_1	kHz	−0.08833(46)	−0.0804	−0.049(18)	−0.052(19)	−0.073(19)	−0.1434(63)	−0.046(19)
d_2	kHz	−0.01874(20)	−0.0401				−0.0258(41)	
rms^b	kHz	2.6		3.0	2.5	3.4	1.8	3.3
N^c		122		18	16	19	17	18

[a] All parameters refer to the principal axis system. Watson's S reduction in I^r representation was used. [b] Root-mean-square deviation. [c] Number of lines.
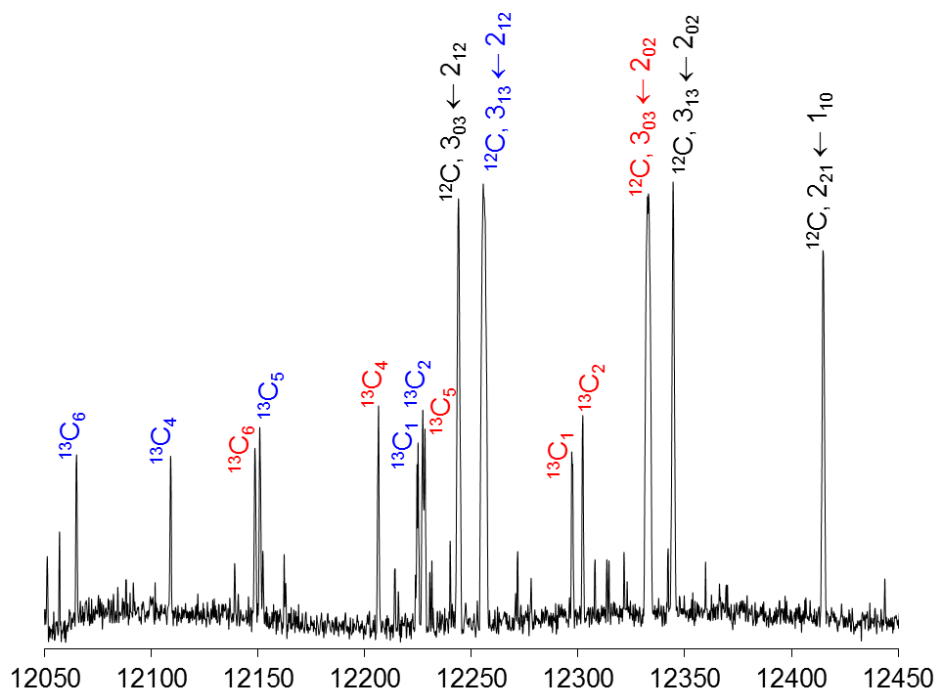
Figure 3. A portion of the experimental survey scan of coffee furanone in the frequency range from 12050 to 12450 MHz. Overlapping spectra are recorded automatically at a step width of 0.25 MHz. For each spectrum, 50 decays were co-added. The intensities are given in a logarithmic scale. Transitions belonging to the parent species (^{12}C) are marked with their respective quantum numbers $J_{K_aK_c}$. The corresponding ^{13}C isotopologues are color-coded with the carbon position given as an index (for atom numbering see Figure 1).

We then suspected that the remaining lines might belong to the ^{13}C-isotopologues of conformer I and calculated the rotational constants of all ^{13}C isotopologues. The four transitions $3_{03} \leftarrow 2_{02}$, $3_{13} \leftarrow 2_{12}$, $3_{03} \leftarrow 2_{12}$ and $3_{13} \leftarrow 2_{02}$ are relatively intense, as visualized in Figure 3, and could be readily assigned for all five ^{13}C species. More lines were subsequently added to the fits, and the rotational constants and three quartic centrifugal distortion constants were well-determined. They are also listed in Table 1 along with the parameters of the parent species. In four

[13]C fits, the d_l parameter is not well-determined, but neglecting this parameter leads to significant deviations of the centrifugal distortion values between the ^{13}C isotopic and the parent species. The assigned transition frequencies are available in Table S-4 in the Supporting Information. To complete the heavy atom structure of coffee furanone, we searched for the two ^{18}O-isotopologues with a natural abundance of 0.2 %. Five promising transitions of the [18]O(3) species could be found and fitted using three rotational constants as given Table S-5 in the Supporting Information. Though we are confident that the fit is correct because the loop formed by four transitions $3_{03} \leftarrow 2_{02}$, $3_{13} \leftarrow 2_{12}$, $3_{03} \leftarrow 2_{12}$ and $3_{13} \leftarrow 2_{02}$ reflects the experimental accuracy, further transitions are too weak to be observed. Therefore, the spectra of the ^{18}O-isotopologues are not considered in the analysis.

The methyl group in coffee furanone undergoes internal rotation with a calculated hindering barrier of 1020 and 1120 cm^{-1} for conformer I and II, respectively. The highest barrier for which resolvable torsional splittings have been observed using a waveguide-FTMW-instrument with a measurement accuracy of 2 kHz (1/10 of the line width at FWHH) is that of ethylchloride with the value of 1234(31) cm^{-1}.[19] In ethyl acetate, the barrier height of one methyl group is 1112.3(37) cm^{-1}, resulting in resolvable splittings for some transitions.[20] The microwave spectrum of on hexan-2-one also revealed splittings arising from the methyl torsion with a barrier height of 1016.30(77) cm^{-1}.[21] However, in the case of coffee furanone, torsional splittings due to internal rotation are only resolvable for some transitions, and caused line broadening of some other transitions. The experimental barrier height cannot be estimated, because not only the torsional barrier but also further factors like the orientation of the methyl rotor and the molecular mass contribute to the order of magnitude of the splittings. Therefore, the internal rotation effect was not considered in the analysis.

4. Discussion

By comparing the rotational constants obtained from the microwave spectrum of the parent species with the predicted ones listed in Table S-2 in the Supporting Information, we find the best agreement with the results calculated at the MP2/6-31G(d,p) level of theory, as also observed for some other molecules such as phenetol[22] and ethyl valerate.[23] In general, the molecular geometry of coffee furanone can be predicted well at all levels of theory, including the cost-efficient Hartree-Fock and Truhlar's M06-2X methods.[24] Surprisingly, rotational constants from calculations at the highest level in use, CCSD/cc-pVTZ, are not in better agreement with the experimental values as those predicted at some lower levels. This is probably due to error compensations. It should be mentioned that the experimental constants A_0, B_0, C_0 are deduced from the ground vibrational spectrum (r_0 structure) and cannot be directly compared with the predicted constants A_e, B_e, C_e, which are calculated at equilibrium (r_e structure). The A_0, B_0, C_0 rotational constants can be obtained from anharmonic frequency calculations, as given in Table 1 (predicted at the MP2/6-311++G(d,p) level of theory). These values are close to the experimental ones; however, they are not in better agreement than the results from the geometry optimizations at the same level of theory (see Table S-2).

The rotational constants deduced from the spectra of the parent species and the five ^{13}C isotopologues allow us to determine the carbon atom microwave structure of coffee furanone. The position of all carbon atoms (referring to the center of mass of the parent isotopologue) can be calculated from the isotopic shifts with Kraitchman's equations[25] using the program *KRA*.[26] The distances to the center of mass are then used to calculate the uncertainties using Costain's rule.[27] Because we can only determine the atom coordinates, the signs have been chosen to be the same as those in the coordinates predicted by *ab initio*. This determined r_s structure, with the carbon

atom coordinates given in Table 2, agrees well with both the ground vibrational r_0 structure and

the vibrational averaged structure (r_z),[28] as illustrated in Figure 4. The Cartesian coordinates of the

r_z geometry are also indicated in Table S-1 in the Supporting Information. Subsequently, the

experimental bond lengths and angles are calculated with the program and $EVAL$[25] and

summarized in Table 3.

$\measuredangle(1,5,4)=103.1(4)°$
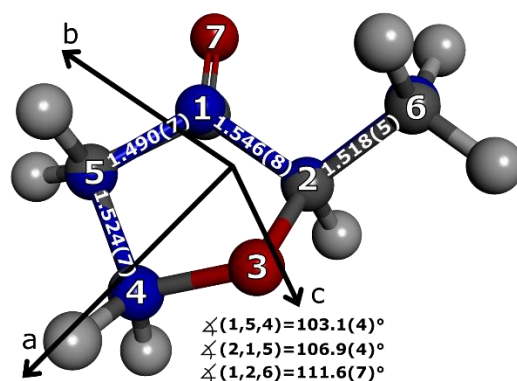$\measuredangle(2,1,5)=106.9(4)°$
$\measuredangle(1,2,6)=111.6(7)°$

Figure 4. Comparison of the carbon atom microwave structure of coffee furanone (r_s, in blue) with

the carbon atom positions (r_z, in gray) of the vibrational averaged structure obtained by anharmonic

frequency calculations. The experimentally deduced bond lengths (in Å) and bond angles (in

degree) are given.

Table 2. Carbon atom coordinates of conformer I of coffee furanone experimentally determined

by ^{13}C isotopic substitutions using the program KRA[26,27] and compared with those of the

vibrational averaged structure (r_z) and the equilibrium structure (r_e).

	Experiment			r_z geometry			r_e geometry		
	a/Å	b/Å	c/Å	a/Å	b/Å	c/Å	a/Å	b/Å	c/Å
C1	−0.3116(49)	0.8271(19)	−0.060(26)	−0.3375	0.8328	−0.0563	−0.3394	0.8256	−0.0547
C2	−0.4517(33)	−0.6450(24)	0.3908(39)	−0.4453	−0.6649	−0.3952	−0.4387	−0.6656	−0.3925
C4	1.78499(84)	−0.2447(62)	0.115(13)	1.7924	−0.2120	−0.1313	1.7848	−0.1995	−0.1371
C5	1.1381(14)	1.0690(14)	−0.3058(50)	1.1214	1.0895	0.3261	1.1113	1.0898	0.3305
C6	−1.64650(91)	−1.3182(12)	−0.2602(58)	−1.6207	−1.3577	0.2763	−1.6069	−1.3596	0.2757

Table 3. Experimental bond lengths and bond angles of conformer I obtained using the program *EVAL*.[26]

Bond lengths / Å		Bond angles / °	
C1−C2	1.546(8)	C1−C2−C6	111.6(7)
C1−C5	1.490(7)	C2−C1−C5	106.9(4)
C2−C6	1.518(5)	C1−C5−C4	103.1(4)
C4−C5	1.524(7)		

The structures of two *twist* conformers of coffee furanone obtained by quantum chemistry, one of which was confirmed by the microwave experiments, are very similar to those of other related five-membered rings found in the literature, which also have two stable *twist* conformers. Figure 2 confirms this observation, where we can recognize that the circles representing stable conformers of 2-methyltetrahydrothiophene (**1**),[13] dihydro-2-methyl-3-thiophenone (**2**),[14] 2-methylcyclopentanone (**3**),[15] and methylcyclopentane (**5**)[10] are almost located at the same positions. This study on coffee furanone again confirms the domination of the *twist* structure over the *envelope* structure, if a carbonyl group is present in the ring. If the carbonyl group is omitted, we obtain 2-methyltetrahydrofuran (**4**), and then the *envelope* structure becomes dominant (see also Figure 2).[16]

5. Conclusion

The conformational analysis of coffee furanone by quantum chemistry leads to two stable conformers with *twist* structures. Under supersonic jet conditions, only the most stable conformer is observed in the microwave spectrum. In addition to the parent species, all ^{13}C isotopologues could be assigned. The fits of all species achieved the measurement accuracy. Using Kraitchman's

equations, bond lengths and bond angles between the carbon atoms were calculated with high accuracy.

ASSOCIATED CONTENT

Supporting Information. Nuclear coordinates in the principal inertial axes of conformer I and II, rotational constants from the basis set variation, frequency lists.

ACKNOWLEDGMENT

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