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Communication through the Furan Ring: Conformational Effect on the Internal Rotation of 5-Methyl Furfural Studied by Microwave Spectroscopy

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Internal rotation is a fundamental motion of end-standing methyl groups that provides important insight on the molecular physics of isolated molecules. The barrier heights of such large amplitude motions are highly sensitive to their molecular and electronic environment. Until now, it is still not possible to accurately determine barrier heights using quantum chemical calculations. To probe for the effect of molecular conformations on the barrier heights of substituted furan rings, the molecular jet Fourier transform microwave spectrum of 5-methyl furfural was recorded in the frequency range from 2 to 40 GHz. Quantum chemical calculations yielded two conformers with a *trans* and a *cis* orientation of the formyl group, which were both observed in the experimental spectrum. Torsional splittings due to the internal rotation of the methyl group were resolved and analyzed. The experimental spectra is reproduced with standard deviations close to the experimental accuracy, yielding sets of highly accurate rotational and internal rotation parameters. The results, especially the V_3 potentials, are compared to quantum chemical calculations and discussed within the scope of the current literature of other methyl substituted furans, where the methyl group is in close proximity of the furan oxygen atom. Our work provides an accurate evaluation of the different case studies and highlights the bottle necks and future options of current available theoretical techniques.

1 Introduction

The title compound 5-methyl furfural (MFF) is a volatile substance also known as 2-furancarboxaldehyde or 5-methyl-2-furaldehyde. It is a pale yellow liquid with a typical almond odour, slightly reminiscent of benzaldehyde¹ and therefore widely used as a flavouring agent in numerous food products. As a furan derivative with a formyl group at the second position and a methyl group at the fifth position of the aromatic ring, MFF features only two degrees of freedoms: the orientation of the formyl group and the internal rotation of the methyl group. While the latter results in three energetically degenerated states, the former yields two different energy minima. Figure 1 shows the structure of MFF with the two possible *cis*- and *trans*-orientations of the formyl moiety.

Since the two degrees of freedoms are not independent, but connected by the conjugated π -system of the ring, MFF is

ideal to study the conformational effects (i.e., the different orientations of the formyl group) on the internal rotation of the methyl group. Predicting the barriers to internal rotation is a difficult task, since chemical intuition often fails and quantum chemistry is not yet sufficiently accurate to predict values close to the experimental level. While a deviation of 1 $\text{kJ}\cdot\text{mol}^{-1}$ (about 84 cm^{-1}) already indicates very high quality of the calculations,² the difference is tremendous in the microwave spectra. If the barrier height is low, the experimental transitions might be shifted by hundreds of MHz by a change of less than one cm^{-1} of the potential barrier. To accurately determine the barrier heights, molecular jet Fourier transform microwave (MJ-FTMW) spectroscopy is the method of choice. The experimental results can be used directly to validate theoretical models and to develop new approaches which account for the underlying physical phenomena.

In the present work, we assigned the microwave spectrum of MFF using a combination of MJ-FTMW spectroscopy and quantum chemical calculations, and performed reliable conformational studies of the system. New experimental insights on the favoured orientations of the formyl moiety and accurate values of the barrier to internal rotation of the methyl group were obtained to validate the calculations. These high resolution studies in the gas phase allow for a fundamental understanding of molecular properties without any influence from the environment such as crystal fields or solvent effects. For this reason, understanding the molecular

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Electronic Supplementary Information (ESI) available: nuclear coordinates in the principal axis system of the conformers and frequency lists.

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physics and intramolecular properties of molecules can be extremely useful to fully elucidate changes during solvation (especially the stepwise micro-solvation) and molecular detection within complex environments such as the biological media. On the long run, joined information obtained from such studies will help to push-forward the fields of molecular recognition, where until now prediction of molecular properties and biological activities remains underdeveloped and provides a great challenge. The results on MFF are discussed within the scope of related furans available in the literature.

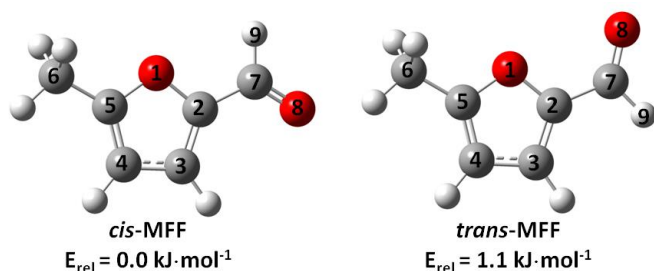


Figure 1. Molecular structures of the two conformers (*cis* and *trans*) of MFF optimized at the MP2/6-311++G(d,p) level of theory. The relative energies in kJ/mol are given with respect to the absolute energy of the lowest energy conformer (*cis*-MFF: $E = -381.617363$ Hartree, including the ZPE correction). For both conformers, the optimizations yielded bond lengths of 1.42 Å for the C4-C3 bond and 1.38 Å for the C4-C5 and the C3-C2 bonds. The value of the C4-C3 bond lengths is thus between those of typical C-C single and double bond length values. This is represented using the single and double bond alternance within the structures.

2 Quantum chemical calculations

The rotation around the C₅–C₆ bond (see Figure 1 for atom labels) corresponds to the internal rotation of the methyl group and does not generate different conformations of MFF. Therefore, the conformational landscape of MFF is determined by the orientation of the formyl group. Through rotation of this group around the C₂–C₇ bond, a potential energy curve was calculated at the MP2/6-311++G(d,p) level of theory using the *Gaussian09* program package.³ Here, the dihedral angle $\varphi_1 = \angle(\text{O}_1, \text{C}_2, \text{C}_7, \text{H}_9)$ was varied in steps of 10°, while all other degrees of freedom were allowed to relax during the optimization process. We chose this level of theory as it has already yielded reliable results in the studies of other substituted furans such as 2,5-dimethylfuran⁴ and 2-acetyl-5-methylfuran.⁵

Altogether, two minima with an energy difference of 0.48 kJ·mol⁻¹ were obtained at dihedral angles $\varphi_1 = 0^\circ$ and $\varphi_1 = 180^\circ$. The potential curve is illustrated in Figure 2, the minima will be henceforward referred to as *cis*-MFF ($\varphi_1 = 0^\circ$) and *trans*-MFF ($\varphi_1 = 180^\circ$). The geometries of these minima were then used as starting points for full optimizations at the MP2/6-311++G(d,p) level of theory. The optimized structures are depicted in Figure 1. Harmonic frequency calculations were subsequently carried out to verify the nature of the stationary points.

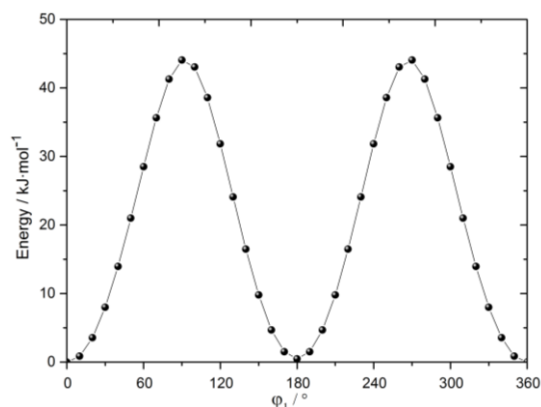


Figure 2. The potential energy curve of MFF obtained by rotating the formyl group around the C₂–C₇ bond, i.e., by varying the dihedral angle $\varphi_1 = \angle(\text{O}_1, \text{C}_2, \text{C}_7, \text{H}_9)$ in a grid of 10° at the MP2/6-311++G(d,p) level of theory. Two stable C_s conformers were found at $\varphi_1 = 0^\circ$ (*cis*) and 180° (*trans*) differ by only 0.48 kJ·mol⁻¹ in energy. The relative energies are given with respect to the lowest energy conformation (*cis*-MFF: $E = -381.7235146$ Hartree).

To have a comparison for the MP2 results, we re-optimized the structures at the B3LYP/6-311++G(d,p) level of theory. For several aromatic rings such as *m*-methylanisole⁶ and 2,3-dimethylanisole⁷ this method has yielded structures with rotational constants closer to the experimental ones which eased the assignment of the microwave spectrum. Both, the MP2 and the B3LYP methods, identified *cis*-MFF as the more stable structure. However, because the energy difference between *cis*-MFF and *trans*-MFF is only about 0.48 kJ·mol⁻¹, an unambiguous distinction is not possible and we expect to observe both conformers in the experimental spectrum. A summary of the results of the quantum chemical calculations is given in Table 1. The Cartesian coordinates of both conformers optimized at the MP2 level are available in Tables S-1 and S-2 in the Electronic Supporting Information (ESI).

Table 1. Rotational constants (in GHz), dipole moment components (in Debye, based on the nuclear coordinates given in Tables S-1 and S-2 in the ESI), relative electronic energies ΔE and relative electronic energies including the zero-point energy correction ΔE_{ZPE} (in kJ·mol⁻¹) with respect to the lowest energy conformer (*cis*-MFF).

	B3LYP/6-311++G(d,p)		MP2/6-311++G(d,p)	
	<i>cis</i> -MFF	<i>trans</i> -MFF	<i>cis</i> -MFF	<i>trans</i> -MFF
A	6.324	4.778	6.243	4.699
B	1.310	1.489	1.312	1.498
C	1.093	1.143	1.091	1.144
μ_a	-4.65	-3.94	-4.73	3.83
μ_b	0.11	2.69	-0.08	3.22
μ_c	-0.00	-0.00	0.00	0.00
ΔE	0.0	2.0	0.0	0.5
ΔE_{ZPE}	0.0	2.2	0.0	1.1

The barriers to internal rotation of the methyl group of both conformers were calculated by varying the dihedral angle $\varphi_2 = \angle(\text{O}_1, \text{C}_5, \text{O}_6, \text{H})$ in steps of 10°. Here, we included additional calculations using the density functional M052X and PBE0

(with and without the Grimme's D3 dispersion correction [8]) to account for the sensitivity of the predicted barrier heights with respect to the applied level of theory. We also calculated the barrier heights at the B3LYP/def2-TZVP and B3LYP-D3/def2-TZVP levels of theory. The correct description of dispersion correction in such methods is extremely important for systems that include weak intermolecular dispersion interactions such as van-der-Waals complexes [9,10]. However, in the case of MFF, there is no significant difference whether the dispersion correction is included or not. Also, we do not see any improvement on the predicted barrier heights obtained at the B3LYP-D3/def2-TZVP level over the values obtained from other methods such as B3LYP/6-311++G(d,p) or M052X/6-311++G(d,p). Table 2 shows an overview of all calculated V_3 potentials. Although they are different for each method, the results clearly indicate an intermediate barrier to internal rotation of the methyl group between 200 cm^{-1} and 350 cm^{-1} . These kind of barrier heights usually leads to observable torsional splittings in the microwave spectrum.

Table 2. Barriers of the internal rotation of the methyl group (in cm^{-1}) of *cis*- and *trans*-MFF calculated at different levels of theory.

	<i>trans</i> -MFF		<i>cis</i> -MFF	
	6-311++G(d,p)	6-311G(d,p)	6-311++G(d,p)	6-311G(d,p)
MP2	334.3	307.4	331.6	309.3
B3LYP	309.1	283.6	310.8	286.2
M052X	332.8	304.6	330.4	302.6
PBE0	262.6	235.7	263.0	237.2
PBE0-D3	260.7	233.7	260.9	235.3
	def2-TZVP		def2-TZVP	
B3LYP	310.4		312.7	
B3LYP-D3	312.7		314.4	

3 Microwave spectroscopy

3.1 Experimental setup

The microwave spectrum of MMF was recorded using two MJ-FTMW spectrometers operating in the frequency ranges from 2.0 to 26.5 GHz¹¹ and 26.5 to 40.0 GHz.¹² A broadband spectrum in the frequency range from 9.0 to 11.0 GHz was first recorded by overlapping spectra with a step size of 0.25 MHz. For all the measurements, a piece of a pipe cleaner of approximately 10 cm length was drained with MFF and mounted upstream of the nozzles in a stainless steel tube of 4 mm inner diameter as described in ref.[13]. Helium was used as a carrier gas and flown over the sample at a pressure of about 150 – 200 kPa. Due to the Joule-Thompson effect upon gas-expansion into the cavity, we assume an extremely low rotational temperature of less than 2 K. We chose helium over heavier carrier gases such as neon or argon, as the molecular beam is usually warmer and typically higher energy conformers can still be detected using this method. However, the number of different conformers that can be detected in the molecular jet largely depends on the barrier heights between these conformers and we do not exclude the possibility that both conformers may also be observed using

neon or argon. Part of the recorded broadband scan is shown in Figure 3. It should also be noted, that due to the low rotational temperature in the molecular jet, excited states of the conformers are not populated and we can therefore only observe rotational transitions in the vibronic ground state of our system. For the characterization of the barrier to internal rotation, this means that the experiment only yields information on the V_3 term of the Fourier expansion of the potential barrier (See also ref.[14] for a more detailed description).

3.2. Spectrum assignment

Quantum chemical calculations have shown that *cis*-MFF is lower in energy than *trans*-MFF (see Section 2). Therefore, the assignment was first attempted using the calculated rotational constants of *cis*-MFF (see Table 1). Due to the high dipole moment in *a* direction, the *a*-type spectrum of *cis*-MFF was calculated in the frequency range from 9.0 to 11.0 GHz using the program *XIAM* in its rigid rotor mode,¹⁵ and compared to the broadband scan mentioned in Section 3.1. *a*-Type transitions are very popular for the assignment of microwave spectra, as they exhibit characteristic patterns which are easy to identify in the spectrum. Here, it should be noted, that the energy potential for the rotation of a methyl group possesses three equal energy minima. If the barrier to internal rotation is sufficiently low, the potential energy takes the shape of a periodic function. In such a case, the degeneracy is partly lifted due to tunneling effects and the energy levels split into in a non-degenerate species and a twofold degenerated species known as the A and the E species, respectively. This leads to torsional splittings in the microwave spectrum, which can be assigned and that yield highly accurate barrier heights for the internal rotation motion of such methyl groups. A more detailed treatment of the theoretical and physical background on internal rotation can be found in refs.[16-19]. A simple introduction to the topic with a more detailed overview of available references is given in ref.[14]. The rigid rotor model, however, neglects this effect and restricts the rotational spectrum to only A species transitions. The general assignment procedure was previously described in ref.[14]. In the case of *cis*-MFF, three transitions $4_{14} \leftarrow 3_{13}$, $4_{04} \leftarrow 3_{03}$ and $5_{15} \leftarrow 4_{14}$ were identified first, which fixed the *B* and *C* rotational constants and enabled the prediction of other *a*-type transitions. Afterwards, *b*-type transitions could be also assigned via trial and error, and the *A* rotational constant was determined as well.

After the successful assignment of the A species, we included the effect of internal rotation into the model and predicted the frequencies of the E species. The angles between the internal rotor axis and the principal axes were taken from the geometry given in Figure 1. Several barrier heights between 200 and 400 cm^{-1} were tried until at $V_3 \approx 350 \text{ cm}^{-1}$ the predicted E species frequencies matched the experimental ones. This enabled us to fit the spectrum of *cis*-MFF with sufficient accuracy to accurately predict additional transitions in the frequency range from 2.0 to 40.0 GHz and improve the

quality of the fit, yielding a more accurate set of rotational and centrifugal distortion constants.

After the spectrum of *cis*-MFF was successfully assigned, a large number of lines remained unassigned in the broadband scan, which should belong to the spectrum of *trans*-MFF. We applied the same procedure described above to assign the spectrum of this conformer. It should be noted that for both conformers no *c*-type transitions were observed due to the C_s symmetry of the molecule. The results of the fits are summarized in Table 3. A complete list of the recorded transitions is given in Tables S-3 and S-4 in the ESI.

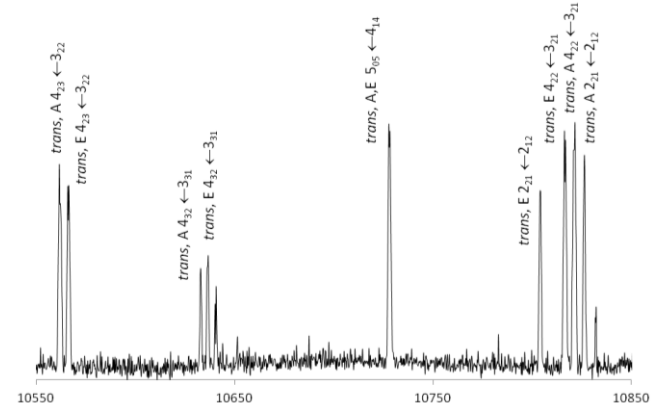


Figure 3. Broadband scan of MFF in the frequency range from 10550 to 10850 MHz. The intensities are given in arbitrary units. In this range, only transitions of *trans*-MFF are present. Each line is labelled by its torsional species and the corresponding quantum numbers of the transition $J', K'_a, K'_c \leftarrow J, K_a, K_c$.

4 Discussion

Using the *XIAM* code, two sets of highly accurate rotational and centrifugal distortion constants were obtained for both conformers of MFF. The fits include the V_3 potential of the methyl group and the angle between the internal rotor axes and the principal *a* axis. In total, 180 and 90 transitions were fitted for *cis*- and *trans*-MFF, respectively. The ratio of the A and the E species transitions in the fits is about 1 : 1. The standard deviation for both fits is 2.2 kHz, which is close the experimental accuracy of about 2 kHz.

The experimental results were directly compared to the constants obtained from *ab initio* calculations given in Table 3, and the experimental sets of rotational constants could be unambiguously attributed to the *cis*- and *trans*-structures obtained from quantum chemistry. The calculated *B* and *C* constants are in almost perfect agreement with the experimental values, whereby the deviations are less than 5 MHz for both conformers. Larger deviations of about 60 MHz (over 1%) are observed for the *A* rotational constants. The orientation of the internal rotor in the principal axis system is also well reproduced by the theoretical calculations.

The torsional barriers of the methyl group predicted at different levels of theory range between 200 cm^{-1} and 350 cm^{-1} and are very similar for the *trans* and the *cis* conformer. The differences are within 5 cm^{-1} at all levels. All calculated values are lower than the experimental V_3 potentials of 358.777(51) cm^{-1} and 352.196(19) cm^{-1} for the *trans* and the *cis* conformer, respectively. The best agreement between the

calculated and experimental barriers for both conformers was obtained using the MP2 method and a triple zeta basis set including the diffuse functions. The less expensive density functional M052X using the same basis set also yielded essentially similar values to those obtain at the MP2 level (see Table 2).

Table 3. Molecular parameters of *trans*- and *cis*-MFF as obtained from the fits using the *XIAM* code.

Par. [a]	Unit	<i>cis</i> -MFF	MP2[b]	<i>trans</i> -MFF	MP2[b]
<i>A</i>	GHz	4.754504(56)	4.699	6.306383(11)	6.243
<i>B</i>	GHz	1.498221038(58)	1.498	1.31483397(13)	1.312
<i>C</i>	GHz	1.147482623(50)	1.144	1.09556256(11)	1.091
Δ_J	kHz	0.12961(46)		0.03725(29)	
Δ_{JK}	kHz	-0.8052(32)		0.2118(76)	
Δ_K	kHz	3.538(17)		–	
δ_J	kHz	0.04260(33)		0.00725(22)	
δ_K	kHz	0.2078(95)		–	
V_3	cm^{-1}	352.196(19)	334.3	358.777(51)	331.5
F_0	GHz	158.0[c]		158.0[c]	
$\angle(i,a)$	$^\circ$	42.236(14)	42.72	26.433(59)	27.17
$\angle(i,b)$	$^\circ$	47.764(14)	47.28	63.567(59)	62.83
$\angle(i,c)$	$^\circ$	90.0[d]	90.00	90.0[d]	90.00
D_{p12K}	kHz	125.0(52)		–	
σ^{e}	kHz	2.2		2.2	
N_A/N_E^{f}		93/87		43/47	

[a] All parameters refer to the principal axis system. Watson's A reduction and I' representation were used.

[b] Calculated at the MP2/6-311++G(d,p) level.

[c] Corresponds to $I_a = 3.2 \text{ u}\text{\AA}^2$, a value often found for methyl groups.

[d] Fixed due to C_s symmetry.

[e] Standard deviation of the fit.

[f] Number of A and E species lines.

Unlike observed in some previous studies on aromatic ring systems such as *m*-methylanisole⁶ or *m*-methylbenzaldehyde²⁰ where significant differences in V_3 potentials between the rotational conformers were observed, the barrier heights of the methyl top for *cis*- and *trans*-MFF are very similar. Obviously, the orientation of the formyl group does not affect the torsional barrier of the ring methyl group significantly. As discussed in ref.[21], there are two factors that affect the height of a methyl rotor torsional barrier: the steric hindrance and the electronic configuration. In the case of MFF, steric effects are absent and the distance between the two substituents implies that electronic properties are more likely to be responsible for the similar barrier heights. Our results suggest that the electronic surrounding of the methyl group is not altered upon the interconversion between the two conformers. This might happen because (i) both conformers have very similar electronic structures or (ii) the electronic interaction between the two substituents through the conjugated π -system in the ring is shielded by the long distance between them or by the oxygen atom. This observation is similar to the situation found for the two conformers in the microwave spectra of 2-acetyl-5-methylfuran,⁵ ethylacetamido-acetate,²² and *n*-pentyl acetate,²³ where almost no change in the barrier height of the methyl group was found for different conformers. However, the barrier heights observed in MFF are clearly lower than the one

found in 2-methylfuran (416.2 cm^{-1}),²⁴ showing that the presence of the formyl group with its negative mesomeric effect and the possibility for an extended π -conjugation may decrease the barrier of the methyl group in MFF.

It is interesting to compare the V_3 potential of the methyl group in MFF with those of other methyl substituted furan derivatives, especially when the methyl group is located in close proximity to the oxygen atom (see Figure 4). Taking the barrier height of 416.2 cm^{-1} of 2-methylfuran (**1**) as a reference,²⁴ the value falls within the range of 350 to 370 cm^{-1} if a formyl or an acetyl group is present at the other side of the oxygen atom in the furan ring, such as it is the case for MFF (**2**) and 2-acetyl-5-methylfuran (**3**).⁵ Both, the formyl and the acetyl group, exhibit a negative mesomeric effect. This kind of electronic distribution in unsaturated compounds induces a polarity due to a transfer of electrons throughout bonds. This is very probably the reason for a decreasing barrier of internal rotation in MFF. The difference between the formyl and the acetyl substituents is not significant. If a methyl group, which has no mesomeric effect, is at the second position of the ring, as is the case of 2,5-dimethylfuran (**4**), the barrier height increases slightly to 439.2 cm^{-1} .⁴ At this stage however, there is still too little data available to establish more precise rules of thumb to predict the barrier height in methyl substituted furans. Further investigations need to be performed, for example on 2-ethyl-5-methylfuran (with the substituent at the second position $R = \text{C}_2\text{H}_5$) to validate whether the length of the alkyl chain affects the barrier height, or on other substituents with $-M$ effect such as 5-methyl-2-furoic acid ($R = \text{COOH}$) or methyl 5-methyl-2-furoate ($R = \text{COOCH}_3$).

The planar moments of inertia $P_{cc} = -2(I_c - I_a - I_b) = 3.190\text{ u}\text{\AA}^2$ and $3.209\text{ u}\text{\AA}^2$ for *cis*- and *trans*-MFF, respectively, confirm that the heavy atom skeleton is planar with a pair of hydrogen atoms situated out of plane. These values are essentially close to those found in the *ap* and *sp* conformers of vinyl methyl ketone ($3.166\text{ u}\text{\AA}^2$ and $3.218\text{ u}\text{\AA}^2$, respectively)²⁵ where the barrier heights are in the same order of magnitude. Comparing this values to other planar molecules containing a methyl group such as the *cis*- and *trans*-conformers of *m*-methylbenzaldehyde ($3.489\text{ u}\text{\AA}^2$ and $3.348\text{ u}\text{\AA}^2$, respectively),²⁰ vinyl acetate ($3.493\text{ u}\text{\AA}^2$),²⁶ and *E*- and *Z*-butadienyl acetate ($3.678\text{ u}\text{\AA}^2$ and $3.540\text{ u}\text{\AA}^2$, respectively),²¹ the planar moments of inertia are also very similar. The deviations arise from different barrier heights in these molecules.

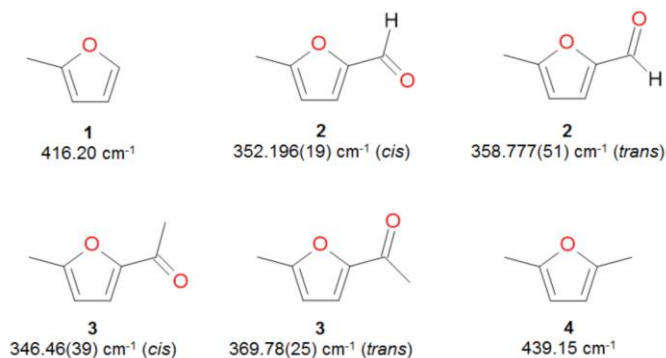


Figure 4. Comparison of the V_3 potentials of MFF (**3**) and related molecules available in the literature: 2-methylfuran (**1**),²⁴ 2,5-dimethylfuran (**2**),⁴ and 2-acetyl-5-methylfuran(**4**).⁵

5 CONCLUSIONS

Two conformers of 5-methylfurfural undergoing internal rotation of the methyl group at the fifth position of the aromatic ring were successfully assigned under molecular jet conditions using a combination of MJ-FTMW spectroscopy and quantum chemistry. Highly accurate molecular parameters were determined. The above mentioned intramolecular dynamics causes torsional splittings of all rotational transitions into the A and E species. The torsional barrier of the ring methyl top is similar in both conformers, showing that the orientation of the formyl group does not influence the barrier height. Comparison to other methyl substituted furans, where the methyl group is in close proximity to the oxygen atom of the furan ring, has shown that the electronic effect has a more significant influence on the methyl barrier height than the conformational (steric) effect. In future, further studies are required to successfully quantify and predict barrier heights for the internal rotation of methyl groups in isolated molecules.

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