

The torsional barriers of two equivalent methyl internal rotations in 2,5-dimethylfuran investigated by microwave spectroscopy

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ARTICLE INFO

Article history:

Received 27 July 2017

In revised form 14 November 2017

Accepted 14 November 2017

Available online 15 November 2017

Keywords:

Microwave spectroscopy

Rotational spectroscopy

Internal rotation

ABSTRACT

The microwave spectrum of 2,5-dimethylfuran was recorded using two pulsed molecular jet Fourier transform microwave spectrometers which cover the frequency range from 2 to 40 GHz. The internal rotations of two equivalent methyl tops with a barrier height of approximately 439.15 cm^{-1} introduce torsional splittings of all rotational transitions in the spectrum. For the spectral analysis, two different computer programs were applied and compared, the *PAM-C_{2v}-2tops* code based on the principal axis method which treats several torsional states simultaneously, and the *XIAM* code based on the combined axis method, yielding accurate molecular parameters. The experimental work was supplemented by quantum chemical calculations. Two-dimensional potential energy surfaces depending on the torsional angles of both methyl groups were calculated and parametrized.

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1. Introduction

The petroleum produced from raw resources is currently threatened by the fossil limits, decreasing accessibility, and hazardous effects on environment. The fulfilment of ever growing needs for petroleum today strongly demands renewable sources. Several studies have shown that the conversion of biomass such as hexose (e.g. fructose or glucose) into liquid fuels is a promising way to produce renewable liquid fuel, with 2,5-dimethylfuran (DMF) as the most attractive product [1,2]. Compared to ethanol known as the unique renewable fuel produced in large quantities so far, DMF promises a distinction by its nearly ideal boiling point (92–94 °C at 1013 mbar) and its high research octane number (RON = 119) [3]. Besides, the energy content of 31.5 MJ/L is similar to that of gasoline (35 MJ/L) and 40% greater than that of ethanol (23 MJ/L) [4]. In addition, it is immiscible with water and easier to blend with gasoline than ethanol.

Despite its widespread use, almost nothing is known about the gas phase molecular structure and internal dynamics of DMF. We considered it worthwhile to study the title molecule by pulsed molecular jet Fourier transform microwave (FTMW) spectroscopy with quantum chemical calculations as a helpful support to obtain this important information. From the structural point of view, DMF

is a derivative of furan with two methyl substitutions on the second and the fifth ring positions. The methyl groups are thus equivalent. Concerning the internal dynamics, when starting this work, we expected that splittings arising from the internal rotations of the two equivalent methyl groups are resolvable. Two programs treating such large amplitude motion problems, the *XIAM* [5] and *PAM-C_{2v}-2tops* codes [6] are applied to reproduce the experimental spectrum. The results obtained from these two codes are compared with each other and with those from quantum chemical calculations.

2. Quantum chemical calculations

2.1. Geometry optimizations

Similar to the case of furan, the heavy atoms of DMF share a symmetry plane because of the π electron delocalization of two conjugated double bonds. This constraint confines the structural analysis to only one starting geometry, which was fully optimized at the MP2/6-311++G(d,p) level of theory using the *Gaussian09* package [7]. In almost all recent investigations we used this method-basis set combination because of its optimal compromise between accuracy and speed of the calculations [8–10]. The optimized structure in the principal axes of inertia is presented in Fig. 1; the nuclear Cartesian coordinates are available in Table S-

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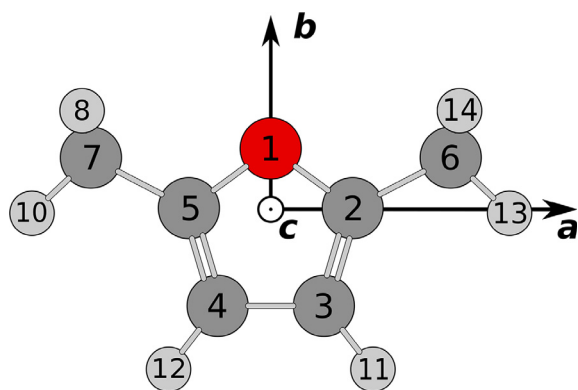


Fig. 1. The equilibrium geometry of DMF optimized at the MP2/6-311++G(d,p) level of theory given in its principal axes of inertia. The direction of the *c*-axis out of the paper plane is indicated by an encircled dot. The protons H₉ and H₁₅ are located behind H₈ and H₁₄, respectively.

1 in the Supplementary Material. Calculations at various combinations of methods (HF, B3LYP, M06-2X, MP2, and CCSD) and Pople and Dunning basis sets [11,12] were performed in addition to check for convergence. The rotational constants obtained at different levels of theory are summarized in Table S-2. All calculated values in the following sections will refer to the MP2/6-311++G(d,p) level, if not stated otherwise.

2.2. Methyl internal rotations

DMF possesses a C_{2v} symmetry and two equivalent methyl rotors. The rotational transitions of such molecule exhibit fine splittings into four torsional components, which can be labeled as (00), (01), (11), and (12) by writing G_{36} as the semi-direct product $(C_3^I \times C_3^I) \times C_{2v}$, as introduced in Ref. [13], where C_3^I is the intrinsic (superscript I) C_3 group of an internal rotor, which is an invariant subgroup of G_{36} . We will use the notation (00), (01), (11), and (12) throughout the present work.

The torsional splittings mainly depend on the orientations of the methyl groups in the molecule and the barriers hindering the internal rotations. While the former can be often calculated well by geometry optimizations, predicting the barrier heights is a much more difficult task. The predicted values vary in a wide range and depend strongly on the level of theory in use [13,14]. A level that yields a reasonable value for one methyl group may fail for another methyl group, even in the same molecule [15]. High level quantum chemical methods such as diffusion quantum Monte Carlo and coupled cluster are more time-consuming, on the other hand are not in better agreement with the experiment than calculations at some levels using the MP2 method [16]. On the other hand, results from quantum chemical calculations often give the correct order of magnitude (low, intermediate, or high) of the barrier heights, which is sufficient to get a start on the spectral assignment.

For DMF, we calculated the barrier heights of the equivalent methyl groups by geometry optimizations to a first order transition state of one methyl group using the Berny algorithm [17] at various levels of theory already mentioned in Section 2.1. The angles between the internal rotor axes and the *a*-principal axis as well as the calculated V_3 potentials are also given in Table S-2 in the Supplementary Material.

2.3. Potential energy surfaces

Two-dimensional potential energy surfaces (2D-PES) depending on the dihedral angles $\varphi_1 = \angle(C_4, C_5, C_7, H_{10})$ and $\varphi_2 = \angle(C_3, C_2, C_6, H_{13})$, corresponding to the internal rotations of the two methyl groups,

were performed at the MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels of theory to study the coupling between the two tops by varying φ_1 and φ_2 in a grid of 10° . Due to symmetry, data points obtained in the range from φ_1 and $\varphi_2 = 0^\circ$ to 120° are sufficient. The corresponding energies were parameterized with a 2D Fourier expansion based on terms representing the correct symmetry. We used the Fourier coefficients summarized in Table S-3 to draw the PES as a contour plot illustrated in Fig. 2. Both PESs exhibit almost no potential coupling terms between φ_1 and φ_2 . The experiment strongly supports this result since no potential coupling terms need to be included in the fits to reproduce the observed rotational spectrum in the ground torsional state to measurement accuracy.

3. Spectral analysis

3.1. The XIAM and PAM- C_{2v} -2tops codes

To analyze the microwave spectra of DMF, we used two different codes which can deal with two-equivalent-top internal rotor problems. The first code is XIAM which has been described in the literature [5]. XIAM uses a combined axis method which sets up the rotation-torsion Hamiltonian in the rho-axis system (RAM) for each top, then converts the RAM parameters into the principal axis system (PAM) parameters.

The second code, PAM- C_{2v} -2tops, has been recently developed to fit the high-resolution torsion-rotational spectra of molecules with two equivalent methyl rotors and a C_{2v} symmetry at equilibrium [6], which was successfully applied to acetone, CH_3COCH_3 [6,18]. It makes use of an explicit 2D potential function and allows simultaneous fitting of rotational transitions belonging to different torsional states of the molecule. PAM- C_{2v} -2tops is based on the G_{36} permutation-inversion (PI) group-theoretical considerations, and uses the principal axis method and a two-step diagonalization procedure. For blockwise diagonalization of a two-top torsion-rotational Hamiltonian, instead of the full G_{36} PI group, the G_9 PI group is used that splits the Hamiltonian matrix into four submatrices corresponding to the (00), (01), (11), and (12) symmetry species. These (00), (01), (11), and (12) blocks correspond to the $(A_1 \oplus A_2 \oplus A_3 \oplus A_4)$, G, $(E_3 \oplus E_4)$, and $(E_1 \oplus E_2)$ symmetry species in G_{36} , respectively. A more detailed description of the program and the underlying group theory can be found in Ref. [6].

3.2. Microwave spectrum

The rotational spectrum of DMF was measured using two molecular jet FTMW spectrometers which cover the frequency range from 2 to 40 GHz. The spectrometer located in Aachen, Germany, operates from 2 to 26.5 GHz [19] and the other one in Paris, France, subsequently from 26.5 to 40 GHz [20]. DMF was purchased from Alfa Aesar GmbH & Co KG, Karlsruhe, Germany, and used without further purification. The stated purity is more than 98%. The substance is a clear, volatile liquid. Its vapor pressure of approximately 50 hPa at $20^\circ C$ is high and therefore simplified the measurement process. For all measurements, we used a gas mixture containing 1% DMF in helium at a total pressure of 60–110 kPa.

The spectrometers can operate in two different modes, the high resolution mode and the scan mode, where a series of overlapping spectra are automatically recorded in a step size of 0.25 MHz, and only the presence of lines is indicated in a broadband scan. In the high resolution mode, all lines appear as doublets due to the Doppler effect with the molecular transition frequency being the center frequency. The splitting depends on both, the frequency range and the velocity of the jet. The estimated measurement accuracy

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