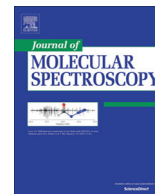




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The microwave spectroscopy study of 1,2-dimethoxyethane

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ABSTRACT

The pure rotational spectrum of 1,2-dimethoxyethane was measured in the 6–18 and 59.6–74.4 GHz frequency ranges using a cavity-based pulsed jet Fourier transform microwave spectrometer and a Stark modulated free-jet millimeter-wave absorption spectrometer, respectively. Two conformers, *TGT* and *TGG'*, have been identified, together with their mono-substituted ¹³C isotopologues. Each rotational transition is split into several components due to the two methyl groups internal rotations. The corresponding *V*₃ barriers have been experimentally determined. MP2/6-311++G(d,p) calculations have provided the determination of the conformational stabilities, structures and spectroscopic parameters.

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1. Introduction

1,2-Dimethoxyethane (DME) is a liquid ether used as aprotic solvent. It has the special ability to form chelates thanks to the high flexibility of its chains. Moreover, DME is the molecular model system for the poly(oxyethylene) chain. In this context, the theoretical and experimental study of its conformations has raised a particular interest over the last years. Several studies in gas and condensed phases are reported aimed at understanding the so called “*gauche* effect” around its C–C bond and the *trans* preference around the C–O bond. NMR and vibrational spectroscopy are the main experimental methods used for these studies [1–5]. There is now a general agreement that in gas phase the *TTT* conformer (the labeling of conformers refers to the positions with respect to the O–C–O chain, see Sketch 1) is the most stable as predicted by *ab initio* calculations, especially when using electron correlation correction and large basis set. However, the same calculations estimate that, at room temperature, also the *TGT* and *TGG'* conformers should be relatively highly populated. These predictions are confirmed by IR spectroscopic studies [6].

As regards the molecule in solution, the experimental techniques led to different conclusion because the population of the *gauche* conformer is enhanced by interacting with strongly polar solvents such as water. In this case, the *TGT* conformer is the lower energy form instead of the *TTT* one. Therefore, *ab initio* calculations

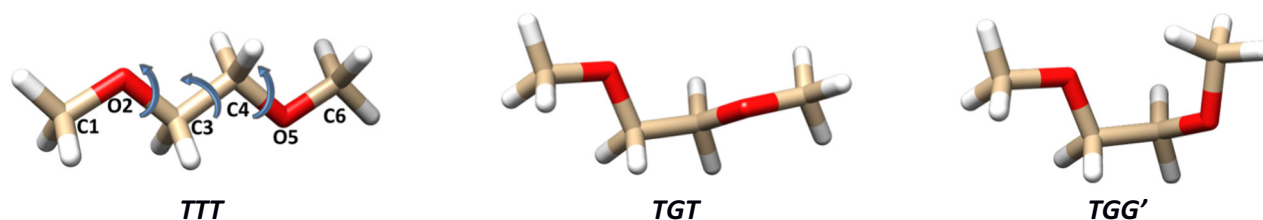
are able to reproduce various gas-phase experimental results whilst they cannot be easily extended to the condensed phase. These conflicting results have driven the development of several theoretical models that could explain the conformational preference of DME as a function of its environments [7,8]. In order to attest the structural features of DME in the isolate phase and to unravel its conformational preferences, we decided to study its rotational spectrum. DME also presents two low energy skeletal torsions which can generate low lying highly populated vibrational states. Hence, in order to investigate its rotational spectrum, we decided to use a Stark modulated free-jet millimeter-wave absorption spectrometer (FJ-MMWA) and a pulsed jet Fourier transform microwave spectrometer (PJ-FTMW) as complementary techniques.

2. Experimental section

Helium at a pressure of ca. 0.22 MPa was flown over a commercial sample of DME (supplied by Sigma–Aldrich and used without further purification) at room temperature. The rotational spectrum was measured in supersonic expansion using a PJ-FTMW spectrometer in a coaxial arrangement of the microwave radiation and of the molecular beam [9], as described previously [10], which covers the range 6–18 GHz. The spectral line positions were determined after Fourier transformation of the 8k data points time-domain signal, recorded with 100 ns sample intervals. Each rotational transition was split by Doppler effect due to the coaxial

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Sketch 1. Mainframes of DME conformers, with the atom numbering and the indication of the dihedral angles generating the various isomers.

arrangement of the supersonic jet and resonator axes. The rest frequency was calculated as the arithmetic mean of the frequencies of the Doppler components. The estimated accuracy of the frequency measurements is better than 3 kHz. Lines separated by more than 7 kHz were resolvable.

Measurements in the 59.6–74.4 GHz frequency range have been performed with a FJ-MMWA spectrometer [11,12]. A gas mixture of DME in argon (ca. 2%) at room temperature was expanded through a nozzle (0.3 mm diameter) from a pressure of 20 kPa to about 0.05 Pa, achieving an estimated rotational temperature of about 10 K. Lines separated by more than 300 kHz are resolvable and the estimated accuracy of the frequency measurements is better than 50 kHz.

3. Theoretical calculations

Before searching the rotational spectra, the spectroscopic parameters of different conformations of DME have been predicted using computational methods. The mainframe structure of DME is described by three dihedral angles (see Sketch 1). All the combinations of the possible values of these dihedral angles can generate $3^3 = 27$ possible rotamers giving 10 non-equivalent molecular configurations. As previously reported [1,7], the complete conformational space of DME has been explored at different levels of computation and taking into account also the effect of intramolecular basis set superposition error [2]. In this work, we have performed new calculations for the structures of the three most stable conformers (namely *TTT*, *TGT*, *TGG'* with the conformational degeneracy of 1, 2, 4, respectively), with the MP2 method at the 6-311++G(d,p) level of theory, using the Gaussian 09 program package [13]. The obtained results with the rotational constants, electric dipole moments components and relative energies, including the zero point corrected ones, are reported in Table 1, as well as the corresponding structural pictures in Sketch 1. The equilibrium structures are listed in the Supplementary Materials. The results

Table 1
MP2/6-311++G(d,p) calculated spectroscopic parameters of DME, and B3LYP/6-311++G(d,p) V_3 energy barriers.

	<i>TTT</i>	<i>TGT</i>	<i>TGG'</i>
A/MHz	18731	10965	6869
B/MHz	1298	1547	2036
C/MHz	1253	1461	1705
$D_J, D_{JK}, D_K/\text{kHz}$	0.59, -0.46, 24.3	0.53, -17.7, 226	0.78, 1.53, 14.8
$d_1, d_2/\text{kHz}$	-0.002, 0.7E-5	-0.09, 0.005	-0.21, -0.025
$ \mu_a /D$	0	0	1.7
$ \mu_b /D$	0	1.5	0.3
$ \mu_c /D$	0	0	0.4
$V_{3_c1}/\text{kJ mol}^{-1a}$	9.87	10.02	9.71
$V_{3_c6}/\text{kJ mol}^{-1a}$	9.87	10.02	6.90
$\Delta E_e/\text{cm}^{-1}$	0 ^b	63	140
$\Delta E_0/\text{cm}^{-1}$	0 ^c	193	215

^a Only the B3LYP/6-311++G(d,p) values are reported.

^b Absolute energy is -308.954892 E_h.

^c Absolute energy is -308.811452 E_h.

indicate that the most stable conformer (*TTT*) has no dipole moment due to its symmetry, and for this reason it cannot be observed by pure rotational spectroscopy. However, the small relative energy difference between the global minimum and the other conformers (less than 3 kJ mol⁻¹) appears promising for the observation of the other species. The potential energy curve for the internal rotation of the two methyl groups have been additionally calculated at the B3LYP/6-311++G(d,p) level of theory in order to predict the possible internal rotation splittings in both conformers. The computational scans were carried out in a step of 5° over the full range of the methyl dihedral angle (HC–OC) was kept fixed at each step whilst all the other structural parameters were freely optimized at each point along the path. The corresponding values of the V_3 energy barriers are reported in Table 1.

4. Rotational spectra

As highlighted before, the theoretical calculations predict the *TTT* conformer (C_{2h} point group) to be the most stable one, but it cannot be observed with our technique due to the lack of a permanent dipole moment. For this reason, we focused on the *TGT* conformer (C_2 point group) and the initial survey scan targeted this form. The first attempt was done using the FJ-MMWA spectrometer, because it allows a fast search in its frequency range. A μ_b -type spectrum was expected and in fact a recognizable pattern of transitions was detected. Looking at the predictions, we first assigned the strongest calculated transitions, belonging to the R -type families $(J+1)_{3,J+1} \leftarrow J_{2,J}$, with J ranging from 4 to 6. Each rotational transition should be split into four component lines, as expected for a molecule with two equivalent internally rotating methyl groups. However, the transitions showed six component lines due to the presence of the “dipole forbidden transitions”. By exploiting this initial assignment, we moved to the PJ-FTMW spectrometer, where we could assign many more R -type rotational transitions and finally also some Q -branch lines. No lines due to μ_a and μ_c dipole moment components have been observed, which is in agreement with the C_2 symmetry of this conformer. The experimental measurements on the *TGT* conformer were later extended to the two ¹³C mono-substituted species observed in natural abundance. These species have a reduced symmetry and, as a consequence, the rotational transitions appeared split into five components.

In the PJ-FTMW spectrum, we could also observe other quite strong transitions that were assigned to the *TGG'* conformer (C_1 point group). For this species, the rotational transitions were split into five components due to the fact that the internal rotors are no longer equivalent. The intensity of the spectrum is such that even in this case we were able to observe the four single mono-substituted ¹³C species in natural abundance. No transitions belonging to other species have been observed in the recorded microwave spectrum. The missing of *TGG'* experimental signals in the FJ-MMWA spectra can be due to different issues. First of all, the intensity of the *TGG'* is predicted to be quite low, because in the 59.6–74.4 GHz frequency range we should observe very high

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