



Microwave spectra of 2-phenylethyl methyl ether and 2-phenylethyl methyl ether-argon: Conformation-dependent tunneling and complexation

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ARTICLE INFO

Article history:

Received 9 November 2017
In revised form 6 December 2017
Accepted 23 December 2017
Available online 4 January 2018

Keywords:

Rotational spectroscopy
Conformer structures
Internal rotation
Quantum chemical calculations
Natural bond orbital analysis

ABSTRACT

High-resolution rotational spectra were recorded for 2-phenylethyl methyl ether and the 2-phenylethyl methyl ether – argon complex using a cavity-based Fourier transform microwave spectrometer. The spectra were assigned to the *ao* and *g⁻ao* monomer conformations and the *g⁻ao* – argon complex. Small tunneling splittings arising from more than one internal motion were resolved for eight transitions of the *ao* conformer; no tunneling splittings were observed in the spectra of the *g⁻ao* conformer or the argon complex. The calculated barriers (ω B97XD/6-311++G(d,p)) for methyl and phenyl internal rotations were found to be very similar for both conformers. The observation of tunneling splittings is limited to the *ao* conformer by relatively large barriers for the internal motions and sensitivity to the rotor axis angles within the two conformers.

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1. Introduction

Conformational flexibility has a significant effect on the physical properties of a compound. 2-Phenylethyl methyl ether (2PME) is a molecule with a flexible structure due to the C–C and C–O single bonds in its alkyl chain; see Fig. 1. 2PME has a terminal methyl group, which may undergo hindered rotation (methyl torsion), and an aromatic ring, which facilitates non-bonded van der Waals interactions. 2PME also has a sizable vapor pressure at room temperature and substantial projections of the dipole moment along principal axes (at least one dipole moment component is greater than 1 Debye in each conformer). These properties make it an excellent molecular system for Fourier-transform microwave (FTMW) spectroscopy to probe different molecular conformations, their van der Waals complexes, and the effects of internal rotations.

Molecular geometry can play a major role in determining the potential barrier to internal rotations such as methyl torsion. Dimethyl ether is a benchmark molecule in the search for the origin of the potential barrier to methyl torsion. In dimethyl ether, Goodman and Pophristic [1] identify three contributions to the 1580-cm⁻¹ potential barrier calculated at the HF/6-31G(2d,p)

level: Pauli steric repulsions, oxygen σ lone-pair reorganization forces, and π interactions between the methyl groups and the oxygen atom. A recent study by our group on the complete series of methyl indoles reemphasizes that the torsional barrier is an overall effect of many individual electronic and steric energy contributions [2]. Electronic contributions include hyperconjugative delocalization interactions of bonding and antibonding orbitals, while steric contributions include local structural changes upon the rotation of the methyl group. Spangler extensively discusses barrier forming factors in methyl torsion for many other molecules [3]. Thus the spatial arrangement of methyl rotors in molecular conformers may affect the torsional barrier.

The present study is the first experimental molecular spectroscopic investigation of 2PME. A significant amount of theoretical and experimental research has been done on similar aromatic and aliphatic ethers with terminal methyl rotors. Reinhold et al. [4] reports the most recent theoretical and rotational spectroscopic study on anisole, the simplest aromatic ether. A two-dimensional relaxed potential scan, along both methyl and methoxy torsional angles, was used to calculate methoxy and methyl torsional barriers to be about 1000 cm⁻¹ and 1200 cm⁻¹ respectively. No methyl torsional splittings have been observed at the spectral resolution of their waveguide-based chirped pulse FTMW spectrometer due to the relatively high barriers. Hayashi et al. [5,6] reported the microwave investigation of trans-ethyl methyl ether. The barrier heights to C–CH₃ and O–CH₃ methyl torsions were determined to be 1154

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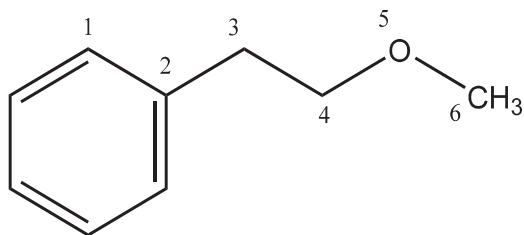


Fig. 1. The numbering scheme used for 2-phenylethyl methyl ether (2PME).

cm^{-1} and 945 cm^{-1} . Microwave spectra of the trans–trans isomer of methylpropyl ether and its 12 isotopically substituted species were reported by Kato et al. [7]. Since the barrier to O–CH₃ methyl rotation was expected to be very high, the observed A–E splittings were explained in terms of C–CH₃ methyl rotation. The calculated C–CH₃ barrier height of $1154 \pm 20.9 \text{ cm}^{-1}$ is close to that of trans-ethyl methyl ether. These surprisingly high potential barriers of O–CH₃ methyl torsion in ether derivatives, which are expected to be much lower because of reduced steric hindrance, have been extensively discussed in the previous work [1,8].

We have investigated microwave spectroscopy and molecular conformations of 2PME and 2PME-argon. This report combines the monomer conformational analysis using ab initio methods, spectral identification of the two most stable conformations, and spectral identification of the most stable van der Waals bonded argon complex. High-resolution cavity spectrometer measurements were useful to resolve the small spectral splittings that arise from high-barrier torsions.

2. Experiment

Rotational spectra were recorded with a 10.5–20 GHz cavity-based FTMW spectrometer [9,10] described in detail earlier [11]. Liquid 2PME (>98%, TCI) was placed in a reservoir nozzle [12] and heated to 120–150 °C using a Watlow band heater and an Omega CN8201 temperature controller. Argon (1.5 atm backing pressure) was passed over the sample and the gas mixture was pulsed into the vacuum chamber using a Series 9 General Valve. A parallel arrangement of the expansion and cavity axis results in Doppler splittings of ca. 60 kHz, as seen in the spectra of the $7_{16}-6_{06}$ transition of the *aoa* conformer and the $8_{08}-7_{07}$ transition of the *g⁻ao* conformer shown in Fig. 2. Typically, the FWHM of Doppler components is about 13 kHz, as shown in Fig. 2B; the digital frequency resolution of the signal is 2.5 kHz.

GAUSSIAN 09 software [13] running on the Oakley cluster of the Ohio Supercomputer Center was employed in all calculations. Electronic structure optimizations and vibrational frequency calculations of the 2PME monomer conformers and 2PME-argon complex were performed to calculate the rotational constants of the equilibrium structures. Full geometry optimizations were performed using the ω B97XD hybrid density functional which includes corrections for long range electron–electron interactions [14]. To further refine energy ordering of individual conformers, the ω B97XD structures were re-optimized at the MP2/6-311++G(d,p) level. Approximate potential barriers to methyl and phenyl torsional motions were calculated for the *aoa* and *g⁻ao* conformers using relaxed potential scans at the ω B97XD/6-311++G(d,p) level. In performing relaxed scans, the dihedral angle was fixed in 15° steps and the remaining structural parameters were optimized.

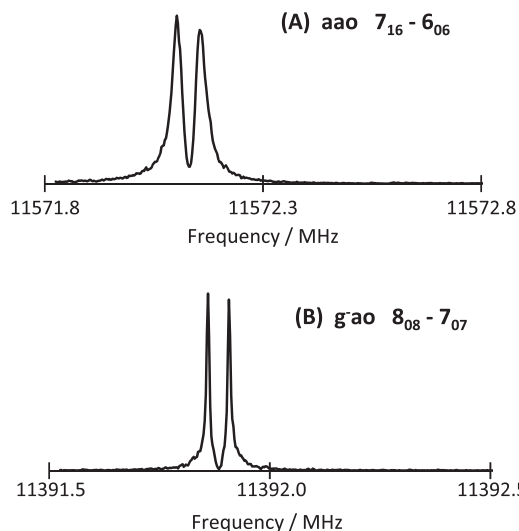


Fig. 2. Portion of the microwave spectrum of 2PME showing Doppler splittings of the (A) $7_{16}-6_{06}$ transition of the *aoa* conformer and (B) $8_{08}-7_{07}$ transition of the *g⁻ao* conformer. Both spectra were recorded by averaging the signal from 250 gas pulses.

3. Results

There are 18 possible conformations of the 2PME monomer that arise from rotation about three bonds. Each of two aliphatic ether dihedral angles, $\angle \text{C}_2\text{C}_3\text{C}_4\text{O}_5$ and $\angle \text{C}_3\text{C}_4\text{O}_5\text{C}_6$ (Fig. 1), gives three different orientations: *anti* (labeled *a*; dihedral angle ca. $\pm 180^\circ$), *gauche⁺* (labeled *g⁺*; dihedral angle ca. $+60^\circ$) and *gauche⁻* (labeled *g⁻*; dihedral angle ca. -60°). The $\angle \text{C}_1\text{C}_2\text{C}_3\text{C}_4$ phenyl dihedral angle gives two orientations: *in-plane* (labeled *i*; dihedral angle ca. $0^\circ, \pm 180^\circ$) and *out-of-plane* (labeled *o*; dihedral angle ca. $\pm 90^\circ$) with respect to the plane defined by C₂, C₃, and C₄. The *g⁻ao* conformation has $\angle \text{C}_2\text{C}_3\text{C}_4\text{O}_5 = -68^\circ$, $\angle \text{C}_3\text{C}_4\text{O}_5\text{C}_6 = 175^\circ$ and $\angle \text{C}_1\text{C}_2\text{C}_3\text{C}_4 \sim 90^\circ$.

The full geometry optimizations at the ω B97XD level converged from 18 starting structures into 8 stable conformations, Fig. 3. Rotational constants, dipole-moment projections, and relative energies of the ω B97XD optimized structures are listed in Table 1. Of these 8 conformations, 6 are comparatively high in energy ($\geq 3.8 \text{ kJ mol}^{-1}$). In the two most stable conformations, *aoa* and *g⁻ao*, the $\angle \text{C}_3\text{C}_4\text{O}_5\text{C}_6$ dihedral angle is in the *anti*-configuration and the phenyl ring is oriented out of the plane with respect to the C₂C₃C₄ plane. Geometry reoptimization at the MP2 level converted three high energy *in-plane-phenyl* structures (*aii*, *g⁻g⁻i*, and *ag⁻i*) into the respective *out-of-plane-phenyl* configurations, reducing the number of distinct structures to six and with a different energy ordering (Table 1).

The potential energy curves for methyl torsion were calculated for the *aoa* and *g⁻ao* conformations (Fig. 4) using relaxed potential scans at the ω B97XD/6-311++G(d,p) level. These potential energies were parameterized to give V_3 and V_6 terms for methyl internal rotation in *aoa* and *g⁻ao* (Table 1). The three-fold barrier to methyl internal rotation is calculated to be nearly the same for both conformations, 857 cm^{-1} for *aoa* and 838 cm^{-1} for *g⁻ao*. The relative values of the V_6 terms indicates that the potential energy for methyl torsion is more harmonic in the *aoa* conformation than in *g⁻ao*. The potential energy of phenyl torsion was calculated for the *aoa* and *g⁻ao* conformations using the same approach. The potential curves, shown in Fig. 5, are quite broad, and the barrier for the *g⁻ao* conformer is asymmetric for the phenyl group rotating towards and away from the *gauche* ether group. The maximum barrier is 615 cm^{-1} for *aoa* and 556 cm^{-1} for *g⁻ao*.

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