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The pure rotational spectra of the two lowest energy conformers of the asymmetric ether $C_4H_9OC_2H_5$

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ABSTRACT

An experimental study has been performed shedding light on the conformational energies of the asymmetric ether *n*-butyl ethyl ether. Rotational spectroscopy between 7.8 GHz and 16.2 GHz has identified two conformers of *n*-butyl ethyl ether, $C_4H_9OC_2H_5$. In these experiments spectra were observed as the target compound participated in an argon expansion from high to low pressure causing molecular rotational temperatures to be below 4 K. For one conformer, 95 pure rotational transitions have been recorded, for the second conformer, 20 pure rotational transitions were recorded. Rotational constants and centrifugal distortion constants are presented for both butyl ethyl ether conformers. The structures of both conformers have been identified by exploring the multi-dimensional molecular potential energy surface using ab initio calculations. From the numerous low energy conformers identified using ab initio methods, the three lowest conformers were pursued at increasingly higher levels of theory, i.e. complete basis set extrapolations, coupled cluster methods, and also taking into consideration zero point vibrational energies. The two conformers observed experimentally are only revealed to be the two lowest energy conformers when high levels of quantum chemical methodologies are employed.

1. Introduction

The accurate prediction of chemical thermodynamic properties remains an important goal of chemistry and a variety of composite methods have become available as predictive quantum chemical tools [1–7]. At the present time, the goal of thermodynamic energy calculations is to be within 1 kcal/mol of the experimental values. For large, aliphatic organic molecules, i.e. flexible molecules containing more than five non-hydrogen atoms, it is not uncommon for several geometric conformers to be within 0–5 kcal/mol of the lowest energy conformer. For progress in the quantum chemical prediction of thermodynamic properties to occur it is clearly desirable to be able to locate these conformers, and, furthermore, to be certain that the lowest energy conformers are indeed known. In this work we have concerned ourselves with locating potential energy minima for a conformationally complex organic compound, namely *n*-butyl ethyl ether. A related species, *tert*-butyl ethyl ether, has previously been studied using similar techniques as presented here [8]. However, this work contains the first high resolution molecular spectroscopy for the title molecule.

With the instrumentation used in this work, the cooling molecular source typically results in only the lowest energy conformations, i.e. those within ≈4 kJ mol^{-1} of the ground state conformer, being observable [9–13]. Rotational spectroscopic experiments on *n*-butyl ethyl ether contained within a supersonic expansion will produce not only conformational geometric information, but will also shed light on which conformers are the lowest in energy.

2. Experiments

n-Butyl ethyl ether (99% pure) was purchased from Sigma–Aldrich Ltd. and used without further purification. The liquid sample was placed in a 1/4 in. tube about 40 cm behind a solenoid valve. Argon held at a backing pressure of 1.5 bar was bubbled through the liquid prior to passage through the pulsed solenoid valve and into a vacuum chamber held at approximately 10^{-7} bar. This process resulted in a rotationally cold, ≈3 K, pulse of the target molecule stabilized within a matrix of supersonically expanded argon.

A Fourier transform microwave spectrometer utilizing chirps of radiation was then used to record the spectra of the target molecules between 7.8 GHz and 16.2 GHz. This instrument has been described in detail elsewhere [14,15] and is based upon the chirped experiment previously introduced by Pate and coworkers [16–18]. Briefly, the instrument mixes a microwave pulse of frequency ν with a fast (6 μs) linear frequency sweep of DC-1 GHz generating a $\nu \pm 1$ GHz broadband pulse. The pulse is then amplified (5 W) using a solid state amplifier and broadcast onto the supersonically

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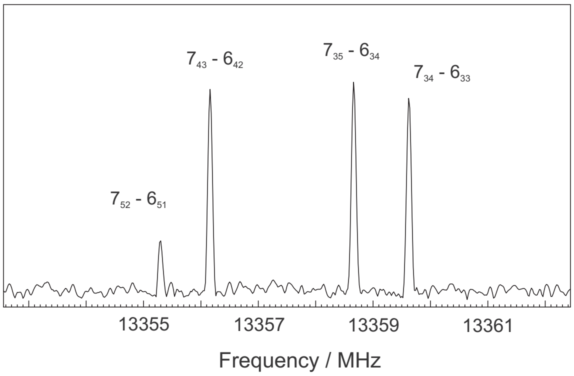

Fig. 1. An approximately 10 MHz section of recorded spectrum for n-$C_4H_9OC_2H_5$. The spectra displayed are the result of 30000 averaging cycles. The a-type transitions shown are carried by Conformer A (see Table 4) and are labeled as $J'_{K_{-1}K_{+1}} - J''_{K_{-1}K_{+1}}$.

Table 1
MP2/6-311G** relative energies, in kJ mol^{-1}, rotational constants, and relative dipole component magnitudes for the five lowest energy conformations of n-$C_4H_9OC_2H_5$.[a]

Conf.	Energy	A/MHz	B/MHz	C/MHz	Rel. Dipole
Conf-I	0.00	6225.4	1013.1	921.5	$\mu_a < \mu_b > \mu_c$
Conf-II	0.11	4656.4	1253.7	1134.1	$\mu_a < \mu_b < \mu_c$
Conf-III	3.50	12363.7	798.8	772.0	$\mu_a \ll \mu_b \gg \mu_c$
Conf-IV	4.27	4501.2	1342.2	1248.0	$\mu_a \ll \mu_b \mu_c$
Conf-V	4.79	4801.2	1185.6	1053.9	$\mu_a > \mu_b \ll \mu_c$

[a] These are the five lowest energy conformations located in this work.

Table 2
Relative MP2 energies, in units of kJ mol^{-1}, for the three lowest energy conformers of n-butyl ethyl ether[a] as a function of basis set size.

Method	Conf-I	Conf-II	Conf-III	ΔE[b]
MP2/6-311G**	0	0.106	3.498	3.392
MP2/aug-cc-pVDZ	0	0.356	1.873	1.517
MP2/aug-cc-pVTZ	0	0.643	1.594	0.950
MP2/aug-cc-pVQZ	0	0.924	1.555	0.631
MP2/aug-cc-pV5Z	0	1.042	1.564	0.522
MP2/CBS(Q5)[c]	0	1.137	1.572	0.435
MP2/CBS(DTQ5-E)[d]	0	1.148	1.576	0.428
MP2/CBS(DTQ5-P)[e]	0	1.378	1.602	0.223
MP2/CBS-ave[f]	0	1.221	1.583	0.362

[a] These are the three lowest energy conformations located in this work, see Table 1.
[b] ΔE(Conf-III – Conf-II)/kJ mol^{-1}.
[c] 2-point extrapolation using Eq. (1) [28].
[d] 4-point exponential extrapolation using Eq. (2) [29].
[e] 4-point power extrapolation using Eq. (3) [30].
[f] The average of the three CBS extrapolations used.

expanding gas sample through a horn antenna. Following a delay of 0.2 μs a second antenna horn receives any free induction decay(s) (FID). The signal is then passed through an amplification stage and then proceeds to be directly digitized on a 12 GHz, 40 GS/s oscilloscope (Tektronix™ TDS6124 Digital Oscilloscope).

The experimental sequence described above takes place at a rate of 2 Hz, and FIDs were averaged for approximately 30000 acquisitions (three 10000 cycle sequences, averaged together post-experiment). Signal averaged regions of 2 GHz were obtained in 5–6 h. Linewidths for these experiments are approximately 80 kHz and a 8 kHz uncertainty was attributed to line center measurements. An example section of spectra is shown in Fig. 1.

3. Quantum chemical calculations

Quantum chemical calculations were performed to identify the conformations of the molecular species observed experimentally. All calculations were performed using the Gaussian software suite [19]. We note that in order to locate different energy minima on the potential energy surface, the starting geometries are very important. To this end we used a conformer generation tool called OMEGA [20,21]. With approximately 60 distinct starting geometries in hand, optimizations were performed using the MP2 ab initio method [22] with 6-311G** basis sets [23,24]. The energies, rotational constants, and relative dipole moment components of the resulting five lowest energy conformers are presented in Table 1. Frequency calculations demonstrated that all five of the conformers shown are true minima on the potential energy surface. These MP2/6-311G** geometries were used as reference geometries for all subsequent calculations. The energies of the three lowest energy conformers determined using the MP2/6-311G** method were then further examined using (i) larger basis sets, and (ii) higher levels of theory. The cartesian coordinates of these three conformers are provided in supplementary data. In regards to the larger basis sets used, we employed the aug-cc-pVnZ ($n \in$ D,T,Q,5) basis sets [25–27]. We also used extrapolation techniques to approach the complete basis set (CBS) limit. These were (1) the 2-point method of Martin [28]:

$$E_\infty = \frac{(n+3/2)^4}{(n+3/2)^4-(n+1/2)^4}E_{n+1} - \frac{(n+1/2)^4}{(n+3/2)^4-(n+1/2)^4}E_n, \tag{1}$$

where the n refers to the n of the aug-cc-pVnZ basis sets used; (2) the multi-point method of Feller [29]:

$$E_n = E_\infty + be^{-cn}, \tag{2}$$

where E_∞, b, and c are adjustable parameters, and E_∞ should be considered the energy at the complete basis set limit; and (3) the multipoint method of Helgaker et al. [30]:

$$E_n = E_\infty + bn^{-c}. \tag{3}$$

In regards to higher level methodologies, we used the MP4 [31], and CCSD(T) [32] methods, and also the so-called MP2:CC method [33] in which the molecular energy is calculated as:

$$E = E(\text{CCSD(T)/SBS}) + [E(\text{MP2/LBS}) - E(\text{MP2/SBS})], \tag{4}$$

where SBS and LBS refer to a “small basis set” and “large basis set”, repectively. The results of these calculations are presented in Tables 2–4.

4. Results and discussions

4.1. Spectral assignment

A progression of weak b-type, Q-branch transitions, $^bQ_{1,-1}$, was located around 11.7 GHz. Tentative qunatum number assignments to these transitions were performed using Kisiel's AABS package [34], available from the PROSPE website [35]. Pickett's SPCAT/SPFIT suite of programs [36] was then used to fit parameters from a Watson S reduced Hamiltonian [37] to the observed transitions. The Hamiltonian used contained rotational constants and quartic centrifugal distortions constants [38]. The resultant parameters were good enough to locate the first of several b-type, R-branch transitions, namely the $J_{K_{-1}K_{+1}} = 1_{11} - 0_{00}$ transition at approximately $A + C \approx 13083.2$ MHz. In total, 20 b-type transitions were located for this species. Given the transitions located were weak, and it was evident that much stronger transitions were within the spectra, this species was ultimately labeled Conformer B.