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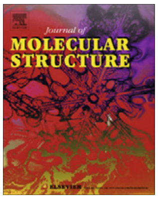

The r_0 structural parameters, conformational stability, barriers to internal rotation, and vibrational assignments for *trans* and *gauche* ethanol

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ABSTRACT

The infrared spectrum (4000–400 cm^{-1}) of the gas and variable temperature (−55 to −100 °C) spectra of xenon solutions of ethanol (ethyl alcohol), CH_3CH_2OH, have been recorded. From these data complete vibrational assignments have been made for both the *trans* (anti) and *gauche* conformers. By utilizing the conformer pair of the CH_3 rock fundamental modes in the xenon solution the enthalpy difference has been determined to be 62 ± 12 cm^{-1} (0.75 ± 0.14 kJ mol^{-1}) with the *trans* form the more stable conformer from variable temperature spectra of xenon solutions. It is estimated that there is approximately $40 \pm 1\%$ of the *trans* form present at ambient temperature. By using the previously reported fifteen rational constants of the five heavy atom isotopomers for the *trans* conformer and the three rotational constants for the *gauche* form combined with the structural parameters predicted from the MP2(full)/6-311+G(d,p) calculations, the adjusted-r_0 parameters have been obtained. The heavy atom structural parameters for the *trans* [*gauche*] are: the distance (Å), C–O = 1.433(3) [1.430(3)], C–C = 1.518(3) [1.523(3)]; and angle (°), CCO = 107.6(5) [112.5(5)], HOCC = 180.0 [56.9(5)]. The Δ_J, Δ_{JK}, Δ_K, δ_J, δ_K centrifugal distortion constants have been predicted from *ab initio* and density functional theory calculations which are compared to the corresponding experimentally determined values. The harmonic force field, infrared intensities, band contours, and vibrational frequencies have been obtained for both conformers from *ab initio* MP2 (full)/6-31G(d) calculations and the results are compared to the experimental values when appropriate. The results are discussed and compared to the corresponding quantities of some similar molecules.

1. Introduction

The conformational stabilities and barriers to internal rotation of alcohols in the gas phase or in solution have provided significant challenges to structural scientist for years for a variety of reasons. The O–H barriers for those that have been determined are about one third or less than those obtained for methyl barriers so there is usually only the fundamental vibration and one excited state in the potential well which makes it difficult to obtain the barriers to internal rotation from the torsional frequencies. Also the determination of the conformational stability has been difficult to determine because of the association due to hydrogen bonding which is significant in the gas phase where vibrations due to the dimer as well as trimers can be observed.

The determination of the structural parameters for ethanol has not been without some serious problems. The first structural determination was an electron diffraction study [1] by Rouault and Gallagher that determined the CC and CO bond distances, the CH bond distances as one set, and the CCO angle. The first complete structural determination was a microwave study [2] where Kadzhar et al. used the principal moments of inertia obtained for ethanol and seven isotopomers to determine the structural parameters. This structural determination suffered from the assumption that the methyl hydrogens were all equivalent and the difference between the secondary moments of inertia $P_{cc}^{-}-P_{cc}$ not being equal to zero. The next complete structural determination was another microwave study [3] by Culot where the rotational spectra of thirteen isotopomers of ethanol were used to determine the r_s structural parameters. In this study [3] it was concluded that the structural determination by the substitution method was unfavorable and the structural parameters obtained were not accurate, this conclusion was based on the finding that the effect of zero-point vibrations is rather large. This effect is even larger when the substitution is done on the in-plane hydrogen atom of the methyl group and the hydrogen atom of the OH group. Culot was aware that the zero-point vibrational effects due to the torsional oscillation of the methyl group resulted in less accurate structural parameters especially those involving the H_7 coordinates, Fig. 4. This was

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followed by two microwave studies by Quade et al. [4,5] where the rotational constants for the *gauche* conformer were determined but no structural parameters were obtained in either study. There are remarkable discrepancies between previously obtained experimental structural parameters of ethanol and the theoretical predicted structural parameters for this molecule. There are also a number of complicating factors which undermine the validity of the structural parameters determined in the previous studies. Additionally, there are currently no structural parameters determined for the *gauche* conformer of ethanol. Therefore, to obtain a more complete determination of the structural parameters for ethanol we have combined the *ab initio* MP2(full)/6-311+G(d,p) predicted parameters with the 18 experimentally determined rotational constants [3,4] for the two forms to obtain the complete structural parameters for both conformers of ethanol.

2. Experiment and theoretical methods

The sample of ethanol was purchased from Sigma–Aldrich Chemical Co., with stated purity of ⩾99%. The sample was further purified by low-temperature, low-pressure fractionation column and the purity of the sample was verified by comparing the infrared spectrum with that previously reported [6].

The mid-infrared spectrum of the gas (Fig. 1A) was obtained from 4000 to 300 cm^{-1} on a Perkin–Elmer model 2000 Fourier transform spectrometer equipped with a Ge/CsI beamsplitter and a DTGS detector. Atmospheric water vapor was removed from the spectrometer housing by purging with dry nitrogen. The theoretical resolution used to obtain the spectrum of the gas was 0.5 cm^{-1}. One hundred twenty-eight interferograms were added and transformed with a boxcar truncation function. The frequencies for the predicted and observed fundamentals for the *trans* and *gauche* conformers are listed in Tables 1 and 2, respectively.

The mid-infrared spectra (4000–400 cm^{-1}) of the sample dissolved in liquefied xenon (Fig. 1B) were recorded on a Bruker model IFS-66 Fourier transform spectrometer equipped with a globar source, a Ge/KBr beamsplitter and a DTGS detector. In all cases, 100 interferograms were collected at 1.0 cm^{-1} resolution, averaged and transformed with a boxcar truncation function. For these studies, a specially designed cryostat cell was used. It consists of a copper cell with a path length of 4 cm with wedged silicon windows sealed to the cell with indium gaskets. The copper cell was enclosed in an evacuated chamber fitted with KBr windows. The temperature was maintained with boiling liquid nitrogen and monitored by two Pt thermo resistors.

The *ab initio* calculations were performed with the Gaussian-03 program [9] using Gaussian-type basis functions. The energy minima with respect to nuclear coordinates were obtained by the simultaneous relaxation of all geometric parameters using the gradient method of Pulay [10]. A variety of basis sets as well as the corresponding ones with diffuse functions were employed with the Møller–Plesset perturbation method [11] to the second order MP2 with full electron correlation as well as with the density functional theory by the B3LYP method.

Table 1
Observed and calculated frequencies (cm^{-1}) for *trans* ethanol.

Sym. block	Vib. No.	Fundamental	*ab initio*[a]	fixed scaled[b]	IR int.[c]	Raman act.[d]	IR gas	Xenon solution	Argon matrix[f]	Raman gas[g]	PED[h]	Band contours[i]	
												A	B
A′	ν_1	OH stretch	3779	3585	22.0	96.6	3676	3648	(3657.6)	3675	$100S_1$	94	6
	ν_2	CH_3 antisymmetric stretch	3211	3012	21.0	54.1	2992	2961	2995.6		$99S_2$	23	77
	ν_3	CH_3 symmetric stretch	3119	2926	11.3	98.6	2922	2920	2939.6		$99S_3$	89	11
	ν_4	CH_2 symmetric stretch	3062	2872	59.7	96.1	2888	2868	2900.5	2887	$100S_4$	–	100
	ν_5	CH_2 symmetric deformation	1598	1503	2.1	5.5	1500	1501	1490.2	1460	$92S_5$	77	23
	ν_6	CH_3 antisymmetric deformation	1567	1472	3.6	22.6	1480	1483	1462.8	1460	$84S_6$	21	79
	ν_7	CH_2 wag	1510	1431	16.8	6.1	1450	1446	1415.0	1430	$54S_7$, $18S_8$, $15S_9$, $10S_{11}$	83	17
	ν_8	CH_3 symmetric deformation	1456	1375	0.9	0.8	1367	1367	(1371.3)		$77S_8$, $19S_7$	80	20
	ν_9	COH bend	1312	1248	83.9	6.6	1241	1238	1240.3	1245	$55S_9$, $16S_7$, $15S_{12}$	52	48
	ν_{10}	CO stretch	1146	1090	18.1	6.1	1090	1086	1091.7	1093	$57S_{10}$, $20S_{12}$	67	33
	ν_{11}	CC stretch	1079	1025	54.6	2.9	1027	1025	1025.0	1026	$51S_{11}$, $21S_9$, $15S_{12}$	69	31
	ν_{12}	CH_3 rock	937	888	11.1	6.1	892	887	886.7	883	$32S_{12}$, $36S_{10}$, $29S_{11}$	70	30
	ν_{13}	CCO bend	427	420	13.1	0.2	418	419	416.5	422	$84S_{13}$, $10S_{12}$	88	12
A″	ν_{14}	CH_3 antisymmetric stretch	3222	3022	21.9	44.1	2987	2965	2985.4		$99S_{14}$	–	–
	ν_{15}	CH_2 antisymmetric stretch	3104	2912	62.4	77.9	2901	2884	2953.5		$99S_{15}$	–	–
	ν_{16}	CH_3 antisymmetric deformation	1550	1455	5.1	16.7	1455	1453	(1445.1)		$93S_{16}$	–	–
	ν_{17}	CH_2 twist	1337	1268	0.2	13.7	1275	1272	(1250.8)		$75S_{17}$, $21S_{19}$	–	–
	ν_{18}	CH_2 rock	1223	1160	4.7	3.6	1166	1156	(1083.2)		$57S_{18}$, $25S_{19}$,$15S_{17}$	–	–
	ν_{19}	CH_3 rock	848	804	0.01	0.04	801	797	(812.1)		$46S_{19}$, $38S_{18}$	–	–
	ν_{20}	OH torsion	316	300	109.0	4.0	202.6[e]		211		$82S_{20}$, $15S_{21}$	–	–
	ν_{21}	CH_3 torsion	265	251	33.8	0.7	244.4[e]		264		$82S_{21}$, $16S_{20}$	–	–

[a] MP2(full)/6-31G(d) predicted values.
[b] MP2(full)/6-31G(d) fixed scaled frequencies with factors of 1.0 for the heavy atom bend, 0.88 for CH stretches and deformations, and 0.90 for all other modes.
[c] Scaled infrared intensities in km/mol from MP2(full)/6-31G(d).
[d] Scaled Raman activities (Å^4/u) from MP2(full)/6-31G(d).
[e] Ref. [7].
[f] Ref. [6], bands marked in parenthesis belong to the *gauche* conformer.
[g] Ref. [8].
[h] Calculated with MP2(full)/6-31G(d) and contributions of less than 10% are omitted.
[i] A, B and C values in the last three columns are percentage infrared band contours.