



Fine structure of far infrared spectrum of ethanol in the lowest OH-torsional vibrational trans-state (e_0) of ethanol



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HIGHLIGHTS

- High Resolution FIR Spectra of Ethanol is being reported for the first time.
- Assignments are confirmed by closed combination loops.
- Torsional overlap matrix elements are calculated to understand the intensity pattern.
- The absence of transitions between the trans- and gauche-shown not to visible.

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ABSTRACT

In this report the spectroscopic results for far infrared Fourier transform spectrum corresponding to the b-type transitions within the lowest lying trans-substrate (e_0) have been presented. The calculated matrix elements connecting various K -levels suggest that $\Delta K = 1$ transitions within the trans-substrate should be quite strong but the transitions between the trans state to the gauche states would quite weak (practically non-existent). This was also concluded by previous studies using microwave and millimeter wave regions (Pearson et al., 1982; Millar, 1995). The assignments were confirmed by direct observations at the spectrum and the agreement between the observed and calculated spectrum using precise energy levels reported by Pearson et al. (1982). All the strong $^R R$ and some $^R Q$ branch lines starting from $K = 10 \leftarrow 9$ through $K = 24 \leftarrow 23$ have been identified. State dependent expansion parameters for all the 15 sub-bands have been presented. These parameters can reproduce the experimental wave numbers within experimental uncertainty. An atlas for about 450 transition lines corresponding to transitions within the e_0 torsional-vibrational species has been prepared. To our knowledge this is the first time the high resolution far infra-red spectral region study for ethanol have been performed.

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1. Introduction

The detailed spectral study of ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) is quite important for many reasons. Firstly, it has been detected in many interstellar clouds and star forming regions [1–3]. Secondly, the molecule has a structure of a near prolate top with two internal rotational degrees of freedom. These make the finer details of energy level structure quite complicated and represent a challenge to spectroscopists. Therefore the spectroscopic study of this molecule is of fundamental importance to understand the intramolecular energy distribution pathways and to provide a laboratory support for interstellar discovery [3–9]. Lastly, ethyl alcohol has a strong absorption band near $10 \mu\text{m}$ region where the strong CO_2 lasers operate. Hence ethyl alcohol can be used as an active

medium for the generation of far infrared (FIR) and Millimeter wave (MMW) lasers, optically pumped by CO_2 lasers. In fact ethyl alcohol and its isotopic derivatives were used to produce substantial number of stimulated FIR emission lines [10,11]. High resolution spectroscopy is a useful tool to identify the quantum numbers involved for the emission lines and to predict new laser line possibilities. The assignments are also important to optimize the efficiency of the emission lines with informed energy level structure involved in the pump and emission process.

The basic understanding of the of the energy level structure and the model of the Hamiltonian have been developed through microwave (MW) studies involving low rotational quantum numbers by Quade and coworkers [4–6]. Later works can be found in Refs. [7–9]. It is noteworthy to mention that Pearson et al. [8] carried out the comprehensive study of the Hamiltonian model using a large number of MMW and MW measured transitions. Their model can reproduce the measured transition frequencies within

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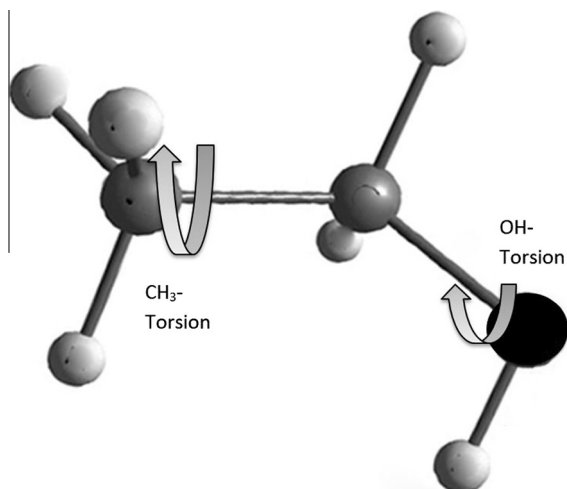


Fig. 1. Schematic of the ethanol molecule.

experimental accuracies. However the Hamiltonian used has quite a huge number of parameters requiring a large CPU time and the physical significance of some of the higher order cross terms is hard to comprehend. On the contrary, the model used by Quade et al. [4–6] is simple and has been extended to higher quantum numbers [12]. Although this model lacks microwave precision but the matrix elements and the energy levels obtained proved to be of immense importance for the identification of various transitions torsional rotational transitions of the prototype molecule CH_2DOH and CHD_2OH for the OH-torsion [see below for the other kind of torsional motion in Ethanol].

In addition to overall rotation and various vibrational modes ethanol has two large amplitude internal rotational motions, viz. the quasi symmetric CH_3 -torsion and the asymmetric OH-torsion, as depicted schematically in Fig. 1. It is known that the CH_3 -torsional barrier potential is quite high (on the order of 1200 cm^{-1}) and produces small splitting in the ground vibrational state. The high barrier causes the wave functions to be highly localized and hence the energy states are not highly mixed [8]. The situation is quite different for the OH-torsion. Here the quantum tunneling effects makes the energy levels highly mixed and thereby making the selection rules somewhat relaxed. In this work the torsional–vibrational energy levels due to OH-torsion is considered. The details of the Hamiltonian model and other calculated quantities can be found in a previous publication [12]. Here only the essential details are briefly discussed in the following section.

2. Theoretical

The asymmetric OH-torsional torsion with respect to the rest of the molecule can be treated to a first approximation as is done for asymmetric methanol species [12]. The energy levels first three levels separate into the trans- (e_0) and the two gauche-states (e_1 and o_1). The mixing of the states arises due to the departure from 3-fold symmetry of the OH-torsion. The inclusion of the terms V_1 and V_2 terms is needed in the hindering potential these makes the torsional–vibrational states to be split and mixed, but unlike asymmetric methanol here the mixing is such that the transitions between the trans- (e_0) to gauche- (e_1 and o_1) are almost nonexistent unless any localized perturbation makes the transition possible through the intensity borrowing effect. However transition within the sublevels of trans-state (a-type and b-type) are quite strong, so as the

Table 1

Matrix elements for lowest trans-state (e_0) to the gauche-states (e_1 and o_1) of ethanol.

	e_0	e_1	o_1
$\langle 10 \mu 9\rangle$			
e_0	0.9489	0.0417	0.0950
e_1	−0.0815	−0.5053	0.8081
o_1	0.0638	−0.8081	−0.4819
$\langle 11 \mu 10\rangle$			
e_0	0.9489	0.0541	0.0881
e_1	−0.0718	−0.5047	0.8086
o_1	0.0742	−0.8086	−0.4812
$\langle 12 \mu 11\rangle$			
e_0	0.9489	0.0655	0.0798
e_1	−0.0611	−0.5045	0.8087
o_1	0.0833	−0.8087	−0.4810
$\langle 13 \mu 12\rangle$			
e_0	0.9489	0.0758	0.0702
e_1	−0.0492	−0.5049	0.8084
o_1	0.0910	−0.8084	−0.4814
$\langle 14 \mu 13\rangle$			
e_0	0.9489	0.0850	0.0594
e_1	−0.0365	−0.5056	0.8078
o_1	0.0974	−0.8078	−0.4824
$\langle 15 \mu 14\rangle$			
e_0	0.9488	0.0927	0.0475
e_1	−0.0230	−0.5068	0.8069
o_1	−0.1021	0.8069	0.4839

transitions between and within gauche- (e_1 and o_1) sub-levels for various K (prolate K value K_p or K_{-1}). This is clearly demonstrated in Table 1, where the overlap torsional matrix element clearly shows that the transitions of the type $e_0 \leftarrow e_0$, $e_1 \leftarrow e_1$, $o_1 \leftarrow o_1$, and $e_1 \leftarrow o_1$ are quite strong, and transitions of the type $e_1 \leftarrow e_0$ or $o_1 \leftarrow e_0$ would be of negligible intensity. Note that among other things the intensity is proportional to the square of the overlap integral in Table 1.

In this report we present the spectroscopic assignments and transition wave numbers in the FIR region for the sub-bands corresponding to quantum transitions between various K -states in the lowest lying trans-species (e_0). All possible $\Delta K = 1$ b-type transitions starting $K = 7e_0 \leftarrow 6e_0$ to $K = 26e_0 \leftarrow 25e_0$ have been detected and in Table 2 we present a catalogue of about 550 FIR transition wavenumbers with their assignments.

3. Experimental aspects

The Fourier Transform (FT) FIR spectra were recorded at the Justus-Liebig Universität in Gießen, Germany, in the range $20\text{--}350\text{ cm}^{-1}$ using a Bruker IFS 120 HR spectrometer. The sample used was spectroscopic grade Ethanol and was used without any further purification. Calibration of the spectra was done using naturally occurring water vapor standard spectral lines. The spectra were recorded at two different temperatures of $-20\text{ }^\circ\text{C}$ and $-60\text{ }^\circ\text{C}$. The operating pressure of the sample was 0.5 mtorr and 0.1 mtorr , respectively. The source used was a mercury vapor lamp designed for the FIR region, and the detector was Si-Bolometer. In both cases the total path length was 3.02 m and 35 scans have been co-added for the spectra recorded at $-20\text{ }^\circ\text{C}$ and spectra at $-60\text{ }^\circ\text{C}$ were obtained by co-adding 180 scans to improve the S/N ratio. Unless otherwise stated the spectra at $-60\text{ }^\circ\text{C}$ have been used throughout this work. The nominal resolution of the spectra was about 0.0018 cm^{-1} . In the experiment mylar beam splitter and polyethylene windows have been used. The complete spectra have been imported into IGOR program and the peak frequencies were obtained by direct observation to reduce any error due to the FTIR peak finding routine.

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