Millimetre-wave spectrum of the singly deuterated isotopologues of *anti*-ethanol

Adam Walters [a,b,*], Mirko Schäfer [c], Matthias H. Ordu [c], Frank Lewen [c], Stephan Schlemmer [c], Holger S.P. Müller [c,*]

[a] *Université de Toulouse, UPS-OMP, IRAP, Toulouse, France*
[b] *CNRS, IRAP, 9 Av. colonel Roche, BP 44346, F-31028 Toulouse cedex 4, France*
[c] *I. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, 50937 Köln, Germany*

ABSTRACT

The rotational spectra of three mono-substituted deuterium isotopologues of the *anti* conformer of ethanol have been measured between 35 and 500 GHz. One of these, CH_2DCH_2OH, exists as two distinct conformers according to the position of the deuterium atom with respect to the molecular skeleton. The dataset was constrained for fitting with a standard Watson-S reduction Hamiltonian by rejecting transitions from high-lying states, which appear to be perturbed by the *gauche* states, and by averaging some small methyl torsional splits. This treatment is compatible with the one we employed for the ^{13}C containing isotopologues of ethanol, and with the needs for a first search for these species in the interstellar medium, in particular in spectra taken by ALMA. For this purpose an appropriate set of predictions is given.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

Ethanol is a near prolate asymmetric top with two large amplitude motions. The methyl internal rotation leads to small splittings that are frequently neglected in spectroscopic analyses. The internal rotation of the OH group has three minima at torsional angles of 180° and ∼±60°. The former leads to the lowest energy *anti* (also known as *trans*) conformer (also known as rotamer), the latter to the doubly degenerate *gauche* conformer. The structure of these two conformers is illustrated in Fig. 1. Tunnelling between the two equivalent *gauche* conformers lifts the degeneracy and leads to the symmetric *gauche+* and the antisymmetric *gauche−* conformers. The lower of the two gauche states, *gauche+*, lies 39.5 cm^{-1} above the *anti* rotamer and 3.3 cm^{-1} below the *gauche−* [1].

Extensive spectroscopic work, in the microwave, millimetre and submillimetre-wave ranges, has been carried out on the parent isotopologue of ethanol. Pearson et al. [1] reported comprehensive measurements and analysis up to 1650 GHz and summarised other published data. For other isotopologues, however, published spectroscopic data are limited and mostly confined to the microwave

region. For this reason we recently reported a study of the millimetre and submillimetre spectrum of the two mono-substituted ^{13}C ethanol isotopologues in the *anti*-configuration [2].

This present work addresses the mono-deuterated isotopologues of the anti conformer of ethanol: CH_3CH_2OD, CH_3CHDOH and CH_2DCH_2OH. The latter exists in two distinct conformers as shown in Fig. 1(a) by the labels *a* and *s*. In the first, the D atom is in the symmetry plane of the molecule, which is hence denoted symmetrical (*s*- henceforth). In the second the deuterium atom is in one of two indiscernible positions such that there is no plane of symmetry and is hence denoted asymmetrical (denoted *a*-); no tunnelling is observed between the two equivalent positions. Hence the spectrum of *a*-CH_2DCH_2OH is expected to be twice as intense as *s*-CH_2DCH_2OH.

Table 1 summarises previous work carried out on the *anti*-rotamer of mono-deuterated ethanol isotopologues. Early work was carried out by Michielsen-Effinger [3] and by Imanov et al. [4,5] for CH_3CH_2OD and CH_3CHDOH, who obtained rotational parameters in the rigid asymmetric molecule approximation, then by Culot [6] for CH_2DCH_2OH. Culot then carried out what was at that time an extensive study of ethanol and its isotopologues and published the results in his doctoral thesis [7]. As regards the mono-deuterated isotopomers he reported 85 transitions for *a*-CH_2DCH_2OH, 72 for CH_3CHDOH, and 72 for CH_3CH_2OD all with $J \leqslant 20$ and below 60 GHz. The data for *a*-CH_2DCH_2OH given in his
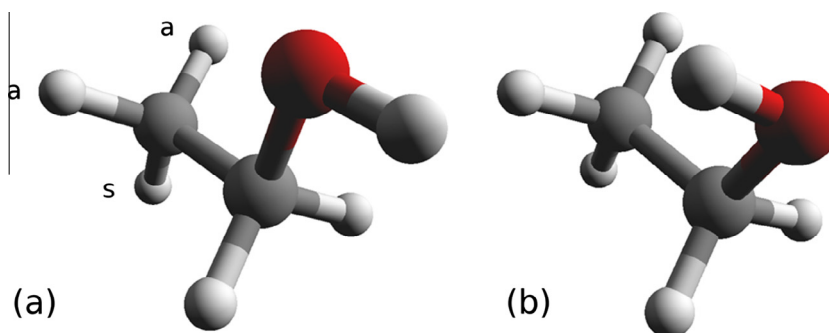
Fig. 1. Structure of the *anti* (a) and *gauche* (b) conformers using *ArgusLab* and based on data given in [1]. The labels "s" and "a" identify the possible substitutions of the deuterium atom in the CH_3 group, respectively, in the plane of symmetry or removing the symmetry.

Table 1
Published results on mono-deuterated anti-ethanol.

	CH_3CH_2OD	CH_3CHDOH	CH_2DCH_2OH	Additionally
Michielsen-Effinger (in French) [3]	7 lines $J \leqslant 7, K_a \leqslant 1$ $\leqslant$45 GHz	7 lines $J \leqslant 7, K_a \leqslant 1$ $\leqslant$45 GHz		Parent, CH_3CD_2OH, $CH_3CH_2^{18}OH$. Gauche
Imanov et al. [4]		8 lines[a] <34 GHz $J \leqslant 5, K_a \leqslant 3$		Parent
Imanov et al. [5]	5 lines[a] <32.5 GHz $J \leqslant 6, K_a \leqslant 3$			$CH_3CH_2^{18}OH$
Culot (in French) [6]			a-CH_2DCH_2OH 85 lines (9[b]) <58 GHz $J \leqslant 20, K_a \leqslant 9$	$CH_3^{13}CH_2OH$ and multiply deuterated species
Sasada et al. [8]		<39 GHz $J \leqslant 5, K_a \leqslant 3$ 11 lines[a]		Gauche. Dipole moment
Culot 1971 (in French) [7]	60 lines (1[b]) <54 GHz $J \leqslant 20, K_a \leqslant 7$	71 lines[a] (8[b]) <55 GHz $J \leqslant 20, K_a \leqslant 8$	s-CH_2DCH_2OH 13 lines[a] (2[b]) <45 GHz $J \leqslant 7, K_a \leqslant 2$	Parent, multiply deuterated species, ^{13}C substitutions, $CH_3CH_2^{18}OH$

[a] Excluding lines found to be wrongly assigned.
[b] Number of lines more than 300 kHz from the latest predictions.

thesis is the same as in the previous article. For s-CH_2DCH_2OH only fourteen transitions were reported and four of these with fitting deviations up to 8 MHz were described as "probable", so that first predictions for this species were less reliable. In particular, centrifugal distortion constants were not well determined.

Sasada et al. [8] measured the microwave spectrum of CH_3CHDOH up to 39 GHz for both the *anti* and *gauche* rotamers, and confirmed that the *anti* rotamer has a plane of symmetry. They also measured the components of the dipole moment by means of Stark spectroscopy. For the *anti* rotamer these are given in Table 2, along with the parent isotopologue, and show that a predominantly *b*-type spectrum is expected. We have found no published values of the dipole moment components for the other isotopologues, but the *b* component is also expected to dominate. Previous results, in particular those of Culot, were invaluable for preparing our study, however, since they do not extend above 60 GHz, these results are not sufficient for predictions for radio astronomy. Kakar and Quade [9] also measured and analysed some lines of the gauche conformers of deuterated ethanol (CH_3CH_2OD, CH_2DCH_2OH and CH_2DCH_2OD) up to 50 GHz maximum.

Culot [7] experimentally determined the relatively large value of the threefold barrier to internal rotation (V_3) of the methyl group for the *anti*-conformer of CH_3CH_2OH, CH_3CH_2OD, CH_3CHDOH (and CH_3CD_2OH). The values obtained for each isotopologue were the same within the supposed uncertainty (less than 2%) with an average of (1160 ± 22) cm^{-1}. Pearson et al. [35] subsequently

Table 2
Published dipole moments for anti-ethanol.

	μ_a	μ_b	μ_c	Ref.
CH_3CH_2OH	0.046 (14)	1.438 (19)	0	[34]
CH_3CHDOH	0.067 (58)	1.519 (6)	0.083 (69)	[8]

determined a value of (1173.8 ± 2.2) cm^{-1} for CH_3CH_2OH. We hence expected torsional splittings for the deuterium isotopologues of generally less than 1 MHz as for the parent and the ^{13}C isotopologues. Indeed, Culot [7] reported splits between 300 and 800 kHz for the low frequency transitions measured. These splits will mostly not be resolved by radio astronomy measurements and hence, as for ^{13}C, we have not carried out a study of the methyl internal rotation in this present work.

Ethanol is observed in several objects in the interstellar medium. The first detection was reported by Zuckerman et al. in 1975 in the giant molecular cloud Sagittarius B2 (Sgr B2) [10]. It has also been identified in the massive star-forming region W51M [11] and the ultra-compact H II region G34.3+0.15 [12]. Lines of ethanol were reported in Orion KL [13,14] and the detection was subsequently confirmed conclusively [15,16]. Lines have also been observed in numerous other star forming regions and hot cores, e.g. [17,18]. Observations indicate that ethanol is principally present in hot core regions with gas densities larger than