A rotational study of the 1:1 adduct of ethanol and 1,4-dioxane

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HIGHLIGHTS

- The microwave spectra of ethanol – 1,4 dioxane adduct and its isotopologue have been measured.
- The hydrogen bond features have been quantified.
- The inverse Ubbelhode effect has been observed.

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ABSTRACT

The pure rotational spectra of the 1:1 ethanol – 1,4-dioxane complex and its OD mono-deuterated species have been measured using pulsed-jet Fourier transform microwave spectroscopy. Conformational predictions for the plausible isomers of ethanol – 1,4-dioxane have been carried out considering the spatial orientation of *gauche*/*trans* ethanol with respect to the *chair*/*boat* and *twisted* conformations of 1,4-dioxane. Using Helium for the supersonic expansion, the microwave spectrum has been observed for the most stable structure. In the observed isomer, the two subunits are linked together by an O—H···O hydrogen bond with *gauche* ethanol acting as proton donor to dioxane in the *chair* conformation. The non-covalent interactions have been characterized using different computational approaches. A small inverse Ubbelohde effect was observed after H → D isotopic substitution in the O—H···O hydrogen bond.

1. Introduction

Solvation phenomena are of pivoting importance in the chemical and biological fields. The solute can interact with the solvent through different types of non-covalent interactions such as (a) polar interactions, (b) van-der-Waals interactions, (c) hydrophobic or apolar interactions and through - most importantly - (d) hydrogen bonds [1]. Obviously, the chemical-physical properties of the solutions are strongly influenced not only by the constituent molecules but also by their interactions and orientations. To understand these complex phenomena, it is necessary to investigate small molecular systems that constitute reference models.

Computational approaches are very popular to study the structure of clusters, wherein one molecule is linked to other molecules through inter-molecular hydrogen bond(s). Some of the most studied systems are water clusters [2,3] and methanol clusters [4,5]. Somewhat surprisingly, the potential energy surfaces of ethanol (EtOH) clusters have been much less explored, probably due to the conformational complexity of the ethanol monomer [6]. In fact, there are three stable structures for the ethanol monomer which are almost isoenergetic: the *trans* (with dihedral angle $\tau_{CCOH} = 180°$) and two degenerate *gauche* structures (g^+ with $\tau_{CCOH} = 60°$ and g^-

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with $\tau_{CCOH} = -60°$) [7]. Microwave spectroscopy is an important experimental tool to investigate the molecular structures. However only a few microwave investigations of ethanol cluster are reported, mainly concerning ethanol dimers, comprising both *trans* and *gauche* forms of the monomer [8,9]. Several other reports concern the 1:1 adducts of water with different alcohols such as ethanol – water [10], isopropanol – water [11], *tert*-butyl alcohol – water [12] and cyclohexanol–water [13]. When the water molecules interact with alcohols to form non-covalent interactions, it generally acts as proton donor.

Another typical organic solvent is 1,4-dioxane (DXN) which is slightly denser than water and acts as a proton acceptor when forming inter-molecular hydrogen bonds. DXN is nonpolar but is soluble in different polar molecules such as water, methanol and ethanol in a wide range of binary mixtures. In binary mixtures, it can play a pivotal role in preferential solvation due to its ambivalent characteristics. Moreover, its ring is flexible and the molecular structure can adopt the *chair*, *boat* and *twisted* conformations. Preferential solvations of solute in different binary mixtures have been outlined in several studies and the thermodynamic properties have been evaluated for several kinds of organic compounds, from simple alkanes, aromatic species such as benzene and toluene, different alcohols (eg. methanol, ethanol and propanol), acetic acid and halogenated compounds [14,15]. However, from a spectroscopic point of view, only a few works have been devoted to binary systems. The literature reports the microwave studies of water – DXN [16,17], *tert*-butyl alcohol – DXN [18] and trifluoromethane – DXN [19]. In these systems the proton donor molecule exhibits only one configuration. No cases are reported where the proton donor molecule participates in a conformational equilibrium. In this study we analyze the pure rotational spectrum of the EtOH – DXN complex, where EtOH provides for two conformers, providing chemical and energetic information on the non-covalent interactions which link the two subunits.

2. Experimental section

The microwave spectra of EtOH-DXN and one monodeuterated isotopologue (EtOD-DXN) have been obtained using a COBRA type pulsed supersonic-jet Fourier Transform Microwave spectrometer (FTMW) [20,21]. The FTMW instrument works in the 6–18 GHz frequency range and has been extensively described elsewhere [22].

In short, the samples, EtOH (98%, b.p. = 351 K) and DXN (anhydrous 99.8%, b.p. = 374 K) are commercially available from Merck and were used without further purification. Rare gas Helium at a stagnation pressure of about 0.5 MPa was flown over two separated reservoirs of EtOH and DXN to reach a stoichiometric ratio of 1:1 in gas phase prior to expansion through a solenoid valve (nozzle diameter 0.5 mm from General Valve Series 9) into the Fabry-Pérot type cavity. A similar procedure has been used for the deuterated isotopologue. Its monomer has been prepared by direct H → D exchange of EtOH with D_2O (purchased from Cambridge Isotope Laboratories), obtaining the EtOD which was used without any further purification.

For each rotational transition the rest frequency is evaluated as the arithmetic average of the frequencies of the two Doppler components deriving from the direction of jet-expansion with respect to the resonator's axis. The estimated accuracy of frequency measurements is 3 kHz.

2.1. Theoretical calculations

Following chemical intuition, the more stable clusters between EtOH and DXN are based by a hydrogen bond interaction between the hydroxyl group of the alcohol and one of the oxygen atoms of the dioxane. However, ethanol exhibits two stable conformers, the *gauche* and the *trans* specie, and can interact with dioxane through the axial and equatorial positions relative to the lone pairs of oxygen. DXN also participates in conformational equilibria despite the chair conformer is calculated to be much more stable than the others. In order to determine all plausible isomers deriving from the interaction of the two subunits (EtOH and DXN) we used a molecular dynamics approach through the Conformer Rotamer Ensemble Sampling Tool (CREST) [23] at the GFN2-xTB level of theory which is available in the extended tight binding (xTB) program package [24]. The initial conformational search led to 131 possible different geometries for EtOH – DXN complex in an energy window of 24.5 kJ/mol. All these 131 isomers have been optimized with B3LYP density functional theory [25] together with D3 dispersion corrections [26] and the Becke–Johnson damping [27] using Ahlrichs' polarized triple-zeta basis set def2-TZVP [28]. This led to the identification of 26 different isomers within an energy windows of 22.7 kJ/mol. Later, all the optimized geometries from B3LYP-D3(BJ) calculations have been re-optimized at different levels of theory using the double hybrid B2PLYPD3 [29] implementing the def2-TZVP basis set and the *ab initio* MP2 methods using the 6-311++G(d,p) basis set [30]. It is worth noting that the higher level calculations reduced the number of different isomers from 26 to 19. The nature of these 19 stationary points has been evaluated by performing vibrational frequency calculations at the harmonic approximation at the B2PLYPD3/def2-TZVP level of theory. This also provided the energy zero-point corrections and the quartic centrifugal distortion constants' estimates. The four most stable conformers lie in an energy interval of 4.2 kJ/mol while an energy jump between conformer 4 and conformer 5 amounts to 10.8 kJ/mol. After adiabatic expansion, all conformers from 5 to 19 will therefore be sparsely populated and cannot be observed experimentally. All the optimizations and frequency calculations were performed using the Gaussian 16 software suite [31]. The results are reported in the supplementary materials (Tables S1–S3).

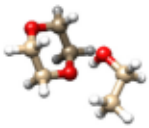
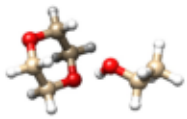
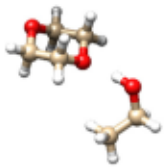
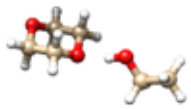
Table 1 reports the spectroscopic parameters utilized in the analysis of the pure rotational spectrum of the four most stable species of EtOH-DXN together with the relative energies accounting for zero-point correction and the dissociation energy (E_D). Table 1 includes sketches of each isomer.

2.2. Rotational spectrum

The isomer of EtOH-DXN predicted to be the most stable exhibits a large μ_c-dipole moment component. For this reason, the first spectral scan has covered a frequency range where its $4_{1,3} \leftarrow 3_{0,3}$ μ_c-type *R*-transition was expected to be found. Using this prediction this intense rotational transition has been identified. Following the pure rotational spectrum pattern many other μ_c-type *R*-transitions (up to $J = 7$) and some weaker μ_b-type and μ_a-type have been observed for a total of 33 measured pure rotational transitions.

The spectrum was not intense enough for the observation of the ^{13}C or ^{18}O species in natural abundance (single substitution). However, the spectrum of the singly deuterated EtOD-DXN isotopologue has been collected and assigned for a total of 24 rotational transitions. The D atom has a nuclear spin $I = 1$, but no splittings due to the rather small deuterium nuclear quadrupole couplings have been observed within our experimental resolution. All measured transitions were fitted using Pickett's SPFIT/SPCAT program suite [32], within the I^r-representation of Watson's *S*-reduction [33]. The final results for the parent and deuterated species are reported in Table 2 with the line lists reported in the supplementary materials (Tables S4 and S5). The experimental rotational constants agree well with the theoretical ones for the most stable

Table 1
B2PLYPD3/def2-TZVP equilibrium and zero point (ZPE) corrected energies and spectroscopic parameters of the first four most stable isomers of EtOH-DXN.

	1	*2*	*3*	*4*
				
ΔE/kJ·mol^{-1}	0, 0 [a, b]	0.6, 0.3	3.2, 2.7	4.2, 3.2
E_D/kJ·mol^{-1}	31.6	31.1	28.4	27.5
A/MHz	2660.5	2737.2	3182.1	4370.6
B/MHz	775.3	674.5	662.4	529.9
C/MHz	746.4	672.9	611.9	494.9
μ_a/D	0.2	0.5	1.5	1.4
μ_b/D	0.6	1.5	0.4	0.0
μ_c/D	1.5	0.0	−1.5	1.8

[a] Absolute energy: E = −462.519523 Eh. [b] Absolute energy + ZPE: E = −462.314060 Eh.

Table 2
Experimental spectroscopic constants of the parent and deuterated EtOD species of EtOH-DXN (*S*-reduction, I^r representation).

	EtOH-DXN	EtOD-DXN
A/MHz	2642.0220(5)[a]	2642.7214(4)
B/MHz	768.3321(2)	767.7155(2)
C/MHz	736.8934(3)	736.1537(2)
D_J/kHz	0.662(3)	[0.662][b]
D_{JK}/kHz	−0.82(2)	[−0.82]
D_K/kHz	8.61(4)	[8.61]
d_1/Hz	−75(1)	[−75]
d_2/Hz	−6.5(7)	[−6.5]
σ[c]/kHz	6.0	11.0
N[d]	33	24

[a] Standard errors in parenthesis are expressed in units of the last digit. [b] Parameters in the brackets are fixed to the values of parent species. [c] Root-mean-square deviation of the fit. [d] Number of fitted transitions.

isomer predicted by the computational calculations. The sketch of the structure with the principal axis systems is shown in Fig. 1. No other predicted isomers have been identified in the microwave spectra.

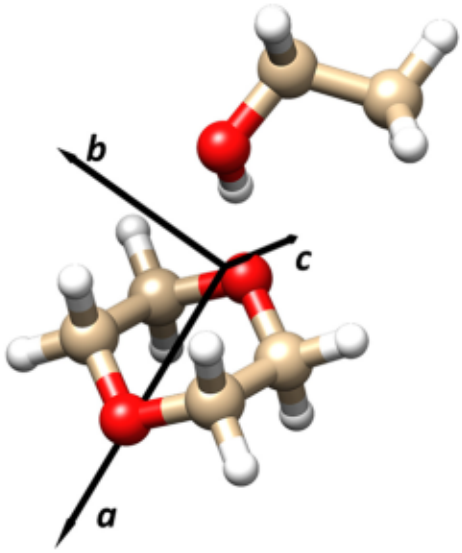


Fig. 1. Sketch of the observed isomer of EtOH-DXN showing the principal axes of inertia.

3. Results

In order to confirm the experimental assignment we estimated the ratio intensities of the dipole moment compontents by measuring the experimental intensities of several nearby rotational transitions following the equations:

$$\frac{\mu_\alpha}{\mu_\beta} = \frac{I_\alpha \gamma_\beta}{I_\beta \gamma_\alpha}$$

where μ is the dipole moment component that must be evaluated for the three components, I represents the measured experimental peak intensities of the choosen rotational transitions and finally γ is the calculated line strenght of the measured experimental rotational transitions without the contribution of the dipole moment components. The line strenght for each rotational transition has been obtained from Pickett's SPFIT/SPCAT program suite [32]. The experimental ratios μ_a:μ_b:μ_c are 1:2.8:7.3 which must be compared with the theoretical ratios calculated at B2PLYPD3/def2-TZVP of 1:3:7.5 as reported in Table 1. It is evident that the experimental data agree with the theoretical prediction for the conformational assignment. Other isomers have not been detected. This is despite the fact that the second isomer is expected to have a population of about 20% of that of the most stable one (which has a double degenerary) and the *trans*-ethanol monomer is observable in the spectrum. Isomer 1 belongs to the C_1 point group and has two degenerate forms because the two *gauche* EtOH (g^+ and g^-) can interact with the DXN subunit at the two equivalent sides. Isomer 2 is formed by EtOH in *trans* form and the complex belongs to the C_s point group. The potential energy surface around the dihedral angle of O1···O2—C3H4, which interconverts isomer 1 to isomer 2, have been computed at the B2PLYPD3/def2-TZVP level of theory in steps of 10°. The dihedral angle has been keep fixed at every step whilst the other geometric parameters that describe the isomer structures were optimized at each point of the path. The plot of the scan is shown in the supplementary material (Fig. S1). The energy barrier determining the interconversion between isomers 1 and 2 was calculated to be 3 kJ/mol. This value is smaller than the barrier of 2kT (~5.0 kJ/mol) required to block such conformational relaxation processes in supersonic expansion. Thus the calculations support the assertion that the second most stable isomer could relax into the lowest energy form.

The non-covalent interactions responsible for intermolecular bonding have been mapped using the NCIPLOT program [34] and are based on a reduced gradient S of the electron density. The results are shown in Fig. 2 for the identified isomer and in the supplementary material for the other three most stable theoretical iso-

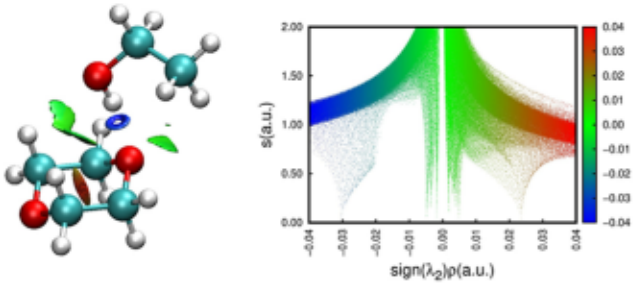


Fig. 2. NCI isosurface for the observed EtOH-DXN isomer. The O—H···O inter-hydrogen bond (area in blue, strongly attractive) is accompanied by weak dispersive interactions (in green) and repulsive zones (in red).

mers (Figs. S2–S4). All the calculated structures exhibit an O—H···O intermolecular hydrogen bond between the two subunits with the ethanol acting as proton donor molecule. The predicted distances of the hydrogen bond for the most stable isomer are r_e = 2.832 Å for O···O and 1.875 Å for OH···O at the B2PLYPD3/def2-TZVP level of theory which are typical for this kind of interactions.

Generally the six-membered rings steer the large groups in equatorial position in order to minimize the steric hindrance and therefore the energy. Interestingly, the two most stable isomers, 1 and 2, exhibit the EtOH subunits which interact with the DXN along the axial configuration. In this case, infact, it is noted that both the *gauche* ethanol and the *trans* ethanol in the two axial conformers present, in addition to the main interaction of the hydrogen bond, two other weakly attractive interactions. These weak interactions, which are shown in green in Fig. 2, are between the lone-pair of alcoholic oxygen and the hydrogens of the DXN structure. In these conformers the distances between O···HC are around 2.8–2.9 Å which falls in the range of weak hydrogen bonds. These weak interactions are not present in the other isomers.

Additional information into these kind of non-covalent interactions have been obtained using the energy decomposition SAPT2+(3)/aug-cc-pVDZ scheme developed in PSI4 package [35]. The results for the EtOH-DXN isomers from 1 to 5 are reported in Table 3.

Isomers 1 to 4 exhibits an inter hydrogen bond as primary interaction, evidenced by the fact that the main interaction is electrostatic (around 53% of the actractive interactions). As previously highlighted, there is an energy jump from isomer 4 upwards. This is due to the fact that the two molecular units do not interact via the hydrogen bond. In these cases, in addition to providing a much weaker binding energy, the SAPT calculation shows that their main component becomes dispersive (about 49% of the total interaction against 27% for the previous conformers) and the electrostatic component decreases dramatically (about 40%).

The predicted theoretical rotational constants (2660, 775 and 746 MHz) are quite close to the experimental data. Microwave spectroscopy is a suited tool to obtain structural information also considering that we have data for the OD mono-deuterated isotopologue. Starting from the calculated isomer (reported in the supplementary material in Table S7) we can obtain an effective structure that is able to reproduce the experimental rotational constants within 0.5% error just increasing of 0.04 Å the O···O inter hydrogen bond length (from 2.83 to 2.87 Å).

Moreover, using the Kraitchman's equations [36] it is generally possible to calculate the substitution coordinates without a priori assumptions [37]. However for this molecular system the equation is unreliable since the inverse Ubbelohde effect might occur and is indeed observed [38,39]. This effect is evidenced by the increase in the value of the rotational constant *A* following the isotopic substitution H → D. The discrepancy can be considerably reduced when we shrink the effective O···O distance by a factor 0.005 Å according to the standard equation for structural fitting [40]. From a physical point of view, the origin of this phenomenon is strictly linked to the different zero-point energies of the hydrogen bond with O—H or O—D [41].

4. Conclusions

We have observed and analyzed the pure rotational spectrum of the EtOH – DXN complex. This isomer is formed by two subunits which are held together by a relatively strong O—H···O inter hydrogen bond between the hydroxyl group of the *gauche* ethanol and the axial lone pair of one oxygen of the *chair* DXN which is acting as proton acceptor. This main intermolecular interaction and the other additional noncovalent interactions between the CH hydrogen in the DXN ring and the lone pairs in the hydroxyl group have been full characterized using NCIPLOT program and the energy decomposition SAPT2+(3)/aug-cc-pVDZ scheme. The computational results show that the nature of the non-covalent interactions is mainly electrostatic for the most stable isomers which have a hydrogen bond. Despite several isomers have been predicted, we missed the observation of the *trans* ethanol or any equatorial isomers, rationalized by relaxation phenomena upon supersonic expansion. As for the equatorial conformers, they lack the secondary interactions stabilizing the axial isomers. Finally, we have also observed and quantified the shrinking of about 5 mÅ related to the inter hydrogen bond upon the H → D isotopic substitution also known as inverse Ubbelohde effect.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Table 3
Results from symmetry-Adapted Perturbation theory (SAPT2+(3)/aug-cc-pVDZ] in kJ/mol.

EtOH-DXN conformer	Electrostatic	Induction	Dispersion	Exchange	Total
1	−46.22	−16.74	−24.43	60.24	−27.14
2	−45.96	−16.61	−22.60	59.19	−25.98
3	−40.40	−14.81	−20.52	51.60	−24.12
4	−40.45	−15.24	−17.80	50.92	−22.57
5	−15.12	−3.94	−18.56	22.37	−15.25

initiative, for the availability of high-performance resources and support.

Appendix A. Supplementary material

1) Completion of Reference 31; 2) Tables of conformational search (Table S2a-S2c); Tables of the transition frequencies (Table S3a and S3b); 3) Atomic coordinates of the isomer 1 of EtOH – DXN; 4) *gauche* to *trans* estimated interconversion barrier of the EtOH – DXN (Figure S1); 5) NCIPlot drawing for isomers 2-4 (Figure S2-S4). Supplementary data to this article can be found online at https://doi.org/10.1016/j.saa.2021.120086.

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