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Conformational changes in hydroxyl functional group upon hydration: the case study of Endo Fenchol

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The hydration of endo-fenchol has been studied in the gas phase using a combination of Fourier transform microwave spectrometer coupled to a supersonic jet expansion and theoretical calculations in the 2 to 20 GHz range. A endo-fenchol...Water complex was observed. Multi-isotopic substitutions of deuterated species have been also studied in order to confirm the identity of the observed monohydrated fenchol due to the flexibility of the OH group. Herein, the structure of the observed conformer was unveiled. Water induced an alteration in the arrangement of the hydroxyl group. The observed species is stabilized by a hydrogen bond between one water molecule and the highest energy conformer of endo-fenchol, which was not observed in our previous study of fenchol monomer.. This study highlights the flexibility of alcohol molecules and the effect of the strong (O-H...O) and weak (C-H...O) hydrogen bonds in the stabilization of the cluster with water.

Introduction

Atmospheric organic aerosols are a complex mixture of fine particles emitted from anthropogenic and biogenic sources.¹⁻³ The emission of biogenic volatile organic compounds (BVOCs) from natural ecosystems have significant impact on chemical and physical properties of the atmosphere, human health and therefore affect the climate.^{4,5} Monoterpenes (C₁₀H₁₆) are hydrocarbons belonging to the BVOC family. Large quantities of monoterpenes are emitted by a variety of plants and coniferous forests into the atmospheric which is estimated to be between 95 to 157 TgC yr⁻¹, a very considerable contribution (about 11%) to the global BVOCs (1150 TgC yr⁻¹)^{6,7}. The degradation of monoterpenes is primarily due to the reaction with OH radical in the daytime and with NO₃ in night-time, and they contribute significantly to the formation of secondary organic aerosols (SOAs)⁸ and tropospheric ozone.^{9,10}

The process of the aerosol formation is still not well understood.¹¹ The first step is the pre-nucleation clusters process by a molecular complex which forms the "critical nucleus" and then grows to a detectable size.^{12,13} Hydrogen bond is one of the main responsible of the formation of atmospheric relevant species. Studies on the formation of SOAs from VOCs and the relation with water presence in the laboratory have been performed.¹⁴⁻¹⁶ It has been shown that the formation of SOA is enhanced by the water presence. In

fact, the relative humidity (RH) plays a very important role in the aerosol formation process, it has been reported that the aerosol quantity increases when the RH increases.¹⁴⁻¹⁶

In a previous work, we reported the study concerning the monoterpene alcohol, fenchol (C₁₀H₁₈O).¹⁷ Fenchol exists naturally in two diastereoisomers forms, endo- and exo-fenchol. Three possible conformers per diastereoisomer were predicted by theoretical calculations but only one conformer¹⁷ was observed for each one. Signals from the observed endo-fenchol conformer were detected to be two orders of magnitude more intense than those from exo-fenchol one, this is could be explained by an excess enantiopure (1R)-endo-(+)-fenchol composition of the purchased commercial samples. To identify the identity of the observed structure of fenchol deuteration species was studied.¹⁷ Only signals from deuterated endo-fenchol were observed and conduct us to identify the observed conformer of endo-fenchol molecule.¹⁷

Fenchol is of atmospheric interest since it has been identified as one of many products emitted from vegetation like Eucalyptus globulus, Cedrus atlantica,¹⁸ radiata pine wood,¹⁹ particleboard and fiberboard.²⁰ Water is one of the most abundant molecules in the Earth atmosphere and humidity is implicated in the aerosols formation.¹⁴⁻¹⁶ In addition, this study is also for special interest to understand how the presence of water that is involved in the hydrogen bond can affect the structure of endo-fenchol. This raises an interesting question: would the hydrogen bond lead to an alteration in the OH group orientation and consequently the stabilization of another form of endo-fenchol? Altogether, it makes interesting to study at the molecular scale the hydrogen bond formed between water and

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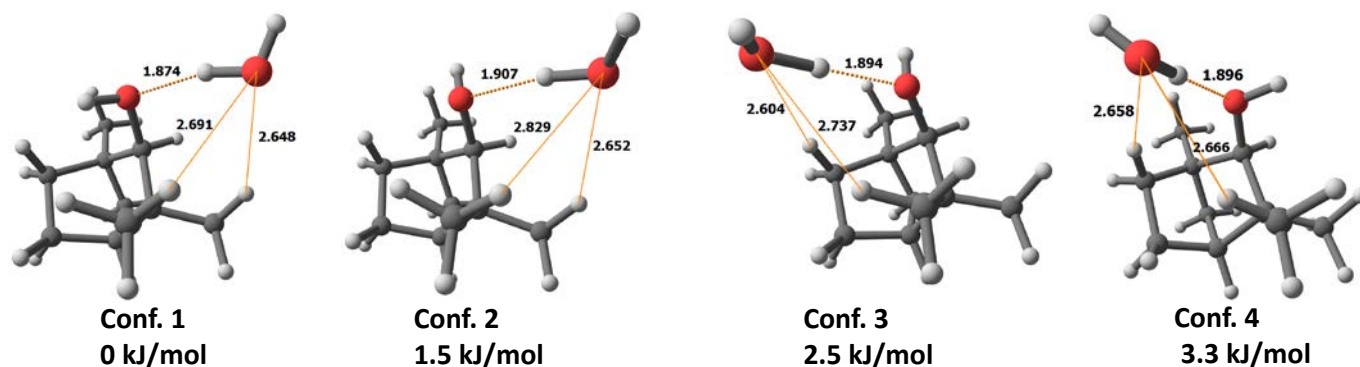


Figure 1. Equilibrium geometries of the lowest energy conformers of EF...water complex calculated at the MP2/6-311++G(d,p) level of theory. The conformers are oriented in the same way to help the visualization of the OH group position of each conformer. The flexibility of the OH group in EF with three different positions allowed the water molecule to complex with EF in four different positions. Relative energies and bond length are indicated for each conformer in kJ/mol and in Å, respectively.

fenchol molecules. Due to the excess of endo-fenchol in the commercial sample, it was only possible to study the micro-solvation of endo-fenchol diastereoisomer (labeled as EF, from now on). Herein we report the study of the EF...water complex. The combination of FTMW spectroscopy with theoretical calculations have been proven to be a powerful tool to study molecular structure and to recognize the observed conformers of fenchol¹⁷ and other molecules in the gas phase.²¹⁻²⁴ Deuterated water was used in order to observe the isotopologue species, which leads to determine the structure of the observed conformer using the substitution method (r_s), this experimental structure is in good agreement with lowest energy conformer predicted by theoretical calculation. Interestingly, the structure found is stabilized by a hydrogen bond linked the water molecule to the non-observed endo-fenchol monomer in its isolated state.¹⁷ This study is relevant to understand the role of hydrogen bonding and its implication in atmospheric chemistry.

Methods

Quantum chemical calculations

Theory is used to predict the conformational molecular properties and to guide the analysis of the rotational spectra.

Theoretical calculations were performed using Gaussian16, Revision B.01, software package.²⁵ The three monomer conformers of EF were considered to form a hydrogen bond with water. The *ab initio* method MP2 (Møller-Plesset second order perturbation theory),²⁶ which gave good results in the study of EF monomer was used in combination with the Pople split-valence triple-zeta basis set augmented with diffuse and polarization functions on all atoms (the 6-311++G(d,p) basis set),^{27,28} to optimize the possible conformers of EF...water complex. The rotational constants (A, B, C), and the quartic centrifugal distortion parameters (Δ_J , Δ_{JK} , Δ_K , δ_J , δ_K) of the Watson's Hamiltonian²⁹ as well as the electric dipole moment components have been calculated for the main species and for the deuterium isotopologues. Structures of the four calculated conformers are shown in Figure 1, and the molecular parameters are reported in the Table 1. Furthermore, to calculate a semi experimental structure of the observed conformer, an optimization using the MP2/cc-PVTZ was performed.³⁰ Using the same method, an analysis of the relevant NBOs involved in the inter-molecular charge transfer responsible of the relative stability of the lowest energy conformer EF...water complex was also performed.³⁰ To plot the map of the interactions involved in the stabilisation of the observed conformer, noncovalent interaction (NCI)³¹ analysis

Table 1. Rotational constants, Relative energies, and dipole moment components of the equilibrium structure of the EF...water complex calculated at MP2/6-311++G(d,p) level of theory.

Parameters ^a	Conf. 1	Conf. 2	Conf. 3	Conf. 4
A	1225.8	1223.6	1004.0	1003.0
B	761.7	763.4	853.6	853.5
C	630.0	632.6	692.9	693.8
ΔE^b	0	1.5	2.5	3.3
$ \mu_a $	2.1	1.8	2.2	2.1
$ \mu_b $	0.4	0.9	0.5	0.7
$ \mu_c $	0.5	0.9	1.5	1.4

^a A, B and C are the rotational constants given in MHz; absolute value of μ_a , μ_b and μ_c are the electric dipole moment components in D (1 D \approx 3.3356 x 10⁻³⁰ C.m); ^b ΔE represents the relative electronic energies in kJ/mol with respect to the global minima calculated at MP2/6-311++G(d,p).

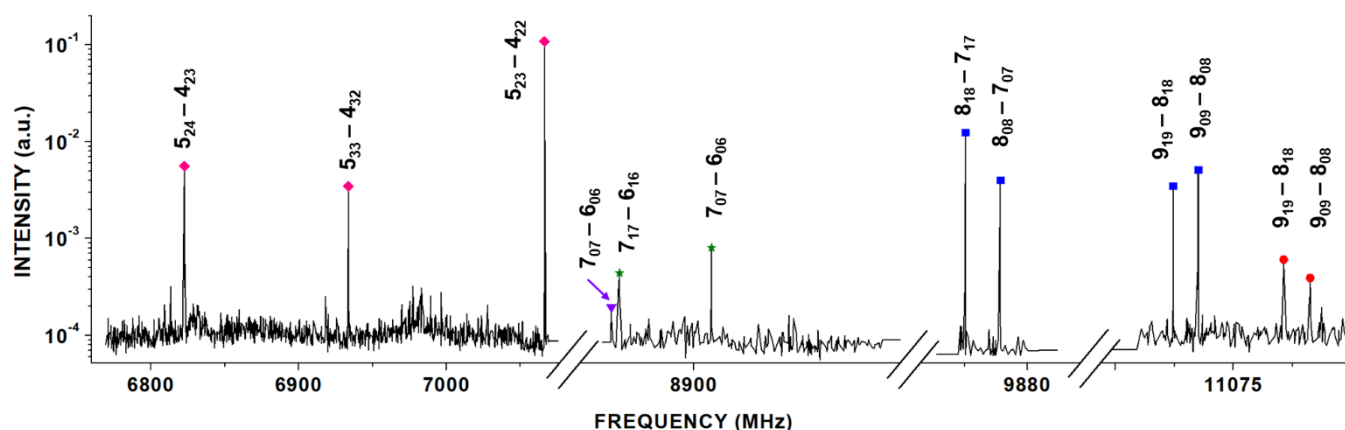


Figure 2. A portion of the low resolution scan spectrum of EF...water complex showing the parent species EF-OH:H₂O in pink rhombus; EF-OH:D₂O in red circle; EF-OD:D₂O in blue square; EF-OH:DOH in olive star; EF-OD:DOH in violet triangle. The EF-OD:HOD is not shown in the figure due to its very weak lines intensities. The intensity is in arbitrary units. The assignment of each rotational line (JK_aK_c) is also indicated.

was carried out using the Multiwfn software³² from the MP2/6-311++G(d,p) level output.

Experimental section

The pure rotational spectrum (2-20 GHz) of EF...water complex was recorded using the Fourier transform microwave spectrometer coupled to a supersonic jet expansion in Lille.^{33,34} Fenchol ($\geq 99\%$ purity) was purchased from Sigma-Aldrich and used without any further purification. Water (H₂O/D₂O) liquid was vaporized in a reservoir placed before the sample. The solid sample of fenchol was heated and vaporized at 373 K to optimize the signal and minimize the decomposition products. A flow of 5 bar of neon was passed through the mixture to create the supersonic jet expansion. The mixture was introduced into a Fabry-Pérot cavity by means of 1 mm diameter pinhole of pulsed nozzle at a repetition rate of 1.5 Hz. The rotational temperature of the molecules in the supersonic

jet is estimated to be a few Kelvin. Microwave power pulses of 2 μ s duration were used to polarize the molecules. The Free-Induction Decay (FID) signals were detected at the heterodyne frequency of 30 MHz and digitized at a repetition rate of 120 MHz. FID signals were accumulated in order to obtain a good S/N ratio.

After the fast Fourier transformation of the time domain signals, lines were observed as Doppler doublets. The central frequency of each line was determined by averaging the frequencies of the two Doppler components. The spectral resolution depends on the number of data points. In our case, the uncertainty of the measurements is estimated to be the better than 2 kHz (1.8 kHz high resolution mode).

Table 2. Rotational constants, quartic centrifugal distortion parameters of EF...water complex, determined experimentally for the ground state, and theoretically from the equilibrium structure.

Parameters ^a	Conf. 1 ^d	EF-OH:H ₂ O	EF-OD:D ₂ O	EF-OD:HOD	EF-OH:D ₂ O	EF-OD:DOH	EF-OH:DOH
A	1225.8	1210.91654(14)	1192.7852(28)	1195.996(28)	1202.3049(17)	1197.554(51)	1207.2160(16)
B	761.7	752.900591(78)	721.01711(21)	729.3201(45)	724.43428(11)	740.397(14)	744.00295(13)
C	630.0	622.335817(60)	599.76547(12)	606.1714(84)	600.80981(12)	614.3054(29)	615.448327(92)
Δ_J	0.0591	0.08308(31)	0.08088(58)	0.0524(32)	0.07899(68)	0.0723(75)	0.08250(41)
Δ_{JK}	0.1470	0.2413(18)	0.198(21)	[0.2413]	[0.2413]	[0.2413]	0.221(12)
Δ_K	-0.0663	-0.1445 (29)	[-0.1445]	[-0.1445]	[-0.1445]	[-0.1445]	[-0.1445]
δ_J	0.00879	0.01322(17)	[0.01322]	[0.01322]	[0.01322]	[0.01322]	[0.01322]
δ_K	0.0448	0.0619(33)	[0.0619]	[0.0619]	[0.0619]	[0.0619]	[0.0619]
σ^b	-	1.7	2.2	0.5	1.8	3.0	1.5
N ^c	-	95	26	7	20	10	27

^a A, B, C are the rotational constants given in MHz; Δ_J , Δ_{JK} , Δ_K , δ_J and δ_K are the quartic centrifugal distortion given in kHz; ^b rms deviation of the fit in kHz; ^c Number of fitted transitions; ^d calculated parameters at MP2/6-311++G(d,p) level of theory. Values between square bracket were kept fixed to those obtain for the parent species.

Results

Molecular parameters

The two predicted conformers 1 and 2 have very close rotational constants and the dipole moments seems to be shared in the same way: strong $|\mu_a|$ dipole moment and two average $|\mu_b| \approx |\mu_c|$. Therefore, the search was started by looking for sets of a-type R-branch transitions ($5_{15} \leftarrow 4_{14}$, $5_{05} \leftarrow 5_{05}$, $6_{16} \leftarrow 6_{16}$, $6_{06} \leftarrow 6_{06}$, $7_{17} \leftarrow 7_{17}$ and $7_{07} \leftarrow 7_{07}$). A single set of these transitions compatible with conformer 1 or 2 was found and fitted successfully. After iterative fittings and predictions, more transitions were found in the spectra and added to the fit of the parent species. About one hundred observed lines were assigned to a-type, and few b-type and c-type transitions of EF...water. Pickett's SPFIT/SPCAT suite of programs³⁵ was used to fit the observed transitions to a Watson's Hamiltonian²⁹ in the I^r representation and in the A -reduction:

$$H_{rot}^{(A)} = B_x^{(A)} J_x^2 + B_y^{(A)} J_y^2 + B_z^{(A)} J_z^2 - \Delta_J J^4 - \Delta_{JK} J^2 J_z^2 - \Delta_K J_z^4 - \frac{1}{2} [\delta_J J^2 + \delta_K J_z^2 - J_z^2]_+$$

The fitted values of the constants, along with the root mean square value on the line frequencies (RMS) are presented in Table 2. Ground state experimental molecular parameter values are compared to theoretically calculated values of the equilibrium position calculated at MP2/6-311++G(d,p).

In contrast to other water complexes with alcohol such as tert-butylalcohol-water,³⁶ or iso-propanol-water³⁷, where some large amplitude motions were observed due to the presence of symmetry, in the rotational spectra of EF...water complex, no splitting associated with internal rotation of the methyl groups or any other large amplitude motion associated to the presence of water were observed.

Alcohols are very flexible molecules, and, in case of EF...water complex, for each position of the water molecule, two orientations of the OH group are possible. Both OH positions do not differ enough to observe significant changes in the rotational constants and dipole moments (see Table 1) that could help us to identify if the specie found corresponds to conformer 1 or 2 based on the criteria. The difference of 1.5kJ/mol between the energy of both species points towards the presence of conformer 1. To be sure of this identification, it is necessary to determine the experimental structure of the observed species by registering the spectra of the deuterated species using D₂O.

About tens of a-type transitions were assigned to the deuterated species: EF-OD:D₂O, EF-OD:HOD, EF-OH:D₂O, EF-OD:DOH and EF-OH:DOH. These transitions have lower signal-to-noise ratio than the parent species. They were fitted also to Watson's Hamiltonian²⁹ in the I^r representation and in the A -reduction. The assignment of the two species EF-OH:HOD and EF-OD:H₂O was not possible.

All the assigned lines of the parent and isotopologues species of EF...water are available in the supplementary material, with the SPFIT output files reformatted with the PIFORM program.³⁸

Molecular structure

Experimental rotational parameters have been obtained for the parent EF-OH:H₂O and for the five substituted deuterium (²H) isotopologues. Six different sets of rotational constants are enough to determine the experimental structure for the hydrogen atoms, and to make possible the confirmation of the identity of the observed conformer. KRA program³⁶ was used for this purpose. The coordinates were calculated using Kraitchman's equations,³⁷ with the uncertainties from vibration-rotation effects as estimated by Costain, and the error on coordinate z is given by $\delta z = 0.0015/|z| \text{ \AA}$.³⁸ This method is called the substitution structure (r_s).

The experimental positions of the hydrogen atoms reported in Table 3 were obtained using different pairs of isotopologues. In case of the H1 atom of EF (see Figure 3), the substitution of EF-OD:D₂O into the EF-OH:D₂O was employed. The outer H3 atom of water, which is free of hydrogen bond, was obtained by substituting the EF-OH:D₂O into EF-OH:DOH, while the hydrogen bonded H2 atom position can be calculated with substitution of EF-OD:D₂O into EF-OD:HOD. The position of hydroxyl hydrogen H1 atom can also be verified by substitution of EF-OD:DOH into EF-OH:DOH. However, similar coordinates were obtained but less accurate than the substitution of EF-OD:D₂O into the EF-OH:D₂O due to the slightly higher error on A and B rotational constants of the EF-OD:DOH complex. Also the position of the outer H3 atom can be verified by another substitution of EF-OD:D₂O into EF-OD:DOH. The results are similar but now slightly less accurate for the c coordinate, which might be caused by the small value of the c coordinate, hence kraitchman's method has problem to determine it. This problem was also reported in our previous structure studies of similar

monoterpenes.^{34,41-42}

As it is observed in Figure 3, the values obtained from the experimental structure are only compatible with the values of

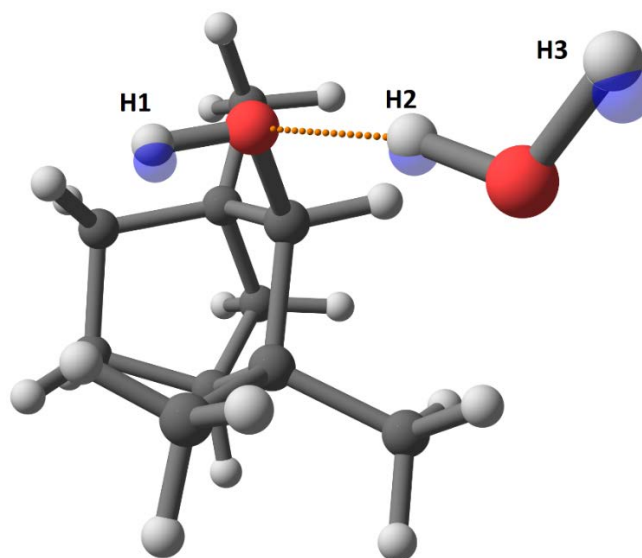


Figure 3. Kraitchman's substitution of three hydrogens in the observed EF...water complex are shown as blue spheres, overlapped to the ab initio structure of conf. 1 calculated at MP2/6-311++G(d,p) level of theory.

Table 3. Comparison between experimental substituted structure (r_s)^a of EF...water complex and *ab initio* equilibrium (r_e)^b of Conf. 1. The (*a*, *b*, *c*) coordinates are given in Å

		<i>a</i>	<i>b</i>	<i>c</i>
H1	r_s	± 0.838(2)	± 0.863(2)	± 1.617(1)
	r_e	- 0.739	1.024	- 1.619
H2	r_s	± 2.800(2)	± 1.030(4)	± 0.330(13)
	r_e	- 2.830	1.103	- 0.329
H3	r_s	± 4.266(1)	± 1.342(1)	± 0.165(9)
	r_e	- 4.218	1.549	0.100

^a Kraitchman's substituted structure; ^b MP2/6-311++G(d,p);

conformer 1, thus, the interaction of fenchol with water alters the position of the alcohol group. As it was reported in the literature,¹⁷ the most stable structure of fenchol monomer is that where the alcohol group points towards the two germinal methyl groups, whereas in the EF...water complex the alcohol group is not anymore oriented in that way, as can be seen in Figures 1 and 3.

This alteration of the OH orientation with the presence of water is also found in other species such as the ethanol-water complexes,⁴³ where the energetically less stable "gauche" conformer becomes the most stable when a hydrogen bond interaction links ethanol to water. Coming back to fenchol, one of the reasons of the reorientation of the hydroxyl group is that the orientation of the OH in Conf. 1 facilitates, not only the formation of the H-bond between the water molecule and the hydroxyl group, but also the presence of two intermolecular interactions between water and the two germinal methyl groups of EF, see straight lines in Figure 1. These two interactions cannot be formed if the OH points towards them, as occur in the most stable monomer of fenchol.¹⁷ To analyse these possible interactions, we obtain the complete semi-empirical structure of EF-water complex and we analyse it with

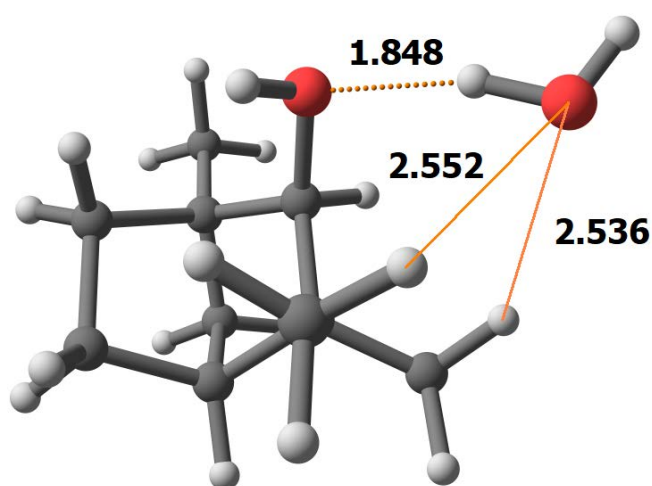


Figure 4. Semi-experimental geometry of the EF...water complex. The experimental determined positions of hydrogen atoms of water and hydroxyl group were fixed and the rest of the structure was optimized using MP2/cc-PVTZ level.

the natural bond orbital (NBO) and non-covalent interactions methods (NCI)³¹.

We observed that the experimental structure of fenchol hydrogen atoms match perfectly with the *ab initio* structure in case of the hydroxyl group and of the hydrogen attached to the oxygen (H1 and H2, respectively), whereas the hydrogen number 3, which is not involved in the hydrogen bond, seems to be little bit lower than its theoretical predicted value and closer to the water oxygen. For that reason, we looked to determine a new semi-experimental structure where the three hydrogen atoms were fixed to the experimental values and the rest of the system was optimized using MP2/cc-PVTZ level of theory, see results in Figure 4. This specie shows a strong hydrogen bond between the $O_{EF} \cdots H_{water}$ ($O1 \cdots H2$) and another two weak hydrogen bonds between $O_{water} \cdots H_{CH_3}$ ($O2 \cdots H22$ and $O2 \cdots H24$) that have the same distance (≈ 2.54 Å) in which the O2 of water is in the mid-distance between both hydrogen (H22 and H24) with an angle $\angle H22O2H24 = 57.5^\circ$.

As it is shown from the observed species, the stability of the Conf. 1 can be traced back to the strong inter-molecular interactions achieved in its structure. Natural bond orbital (NBO) analysis provides an intuitive framework to rationalize the transfer of electronic charge associated with this conformer. We have performed the NBO analysis at MP2/cc-PVTZ on the calculated semi-experimental structure to better understand the preference of this configuration structure. The dominant interaction occurs by a charge transfer between lone pair orbital of the hydroxyl oxygen atom O1 and BD* orbital of H2-O2 of water with a stabilization energy of about 40 kJ/mol. The dispersive stabilisation energies between O2 and the two hydrogen C-H24 and C-H22 ($C-H22 \cdots O2$ and $C-H24 \cdots O2$) of

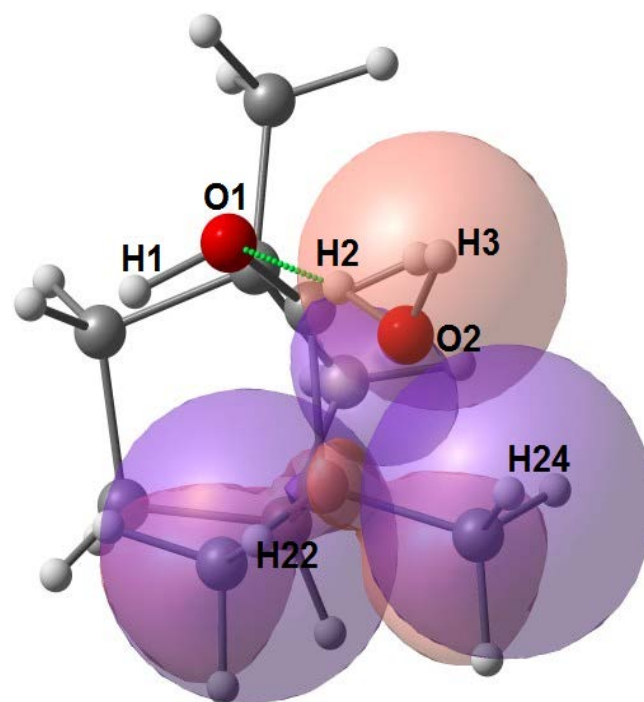


Figure 5. Relevant NBOs involved in the inter-molecular charge transfer responsible of the relative stability of the lowest energy conformer EF...water complex calculated at the MP2/cc-PVTZ level of theory.

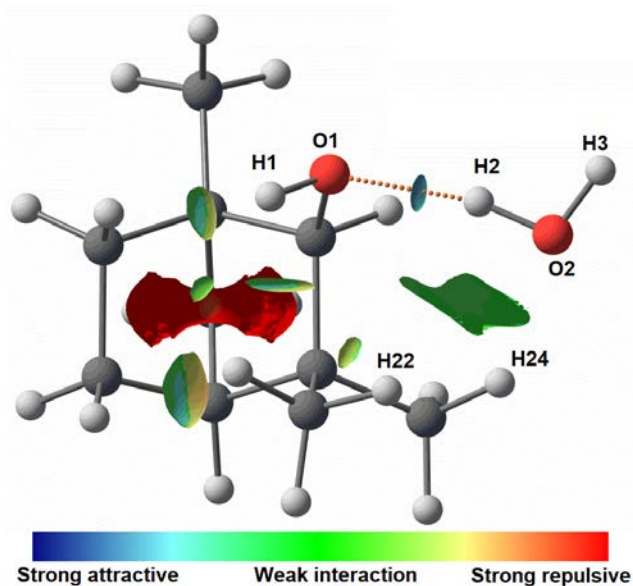


Figure 6. NCI plots showing the interactions involved in the stabilisation of the observed conformer EF...water complex.

methyl groups are calculated to be 2.9 and 1.3 kJ/mol, respectively.

Another interesting analysis can be performed to visualise the interactions involved in the stabilisation of the observed species of fenchol...water complex. The Non-Covalent Interactions (NCI) method³¹ analyses the electron density and its derivatives. This analysis is in good agreement with the NBO analysis and confirms the existence of a strong hydrogen bond and two additional weak hydrogen bonds interaction between water and endo-fenchol. As shown in Figure 6, the dark blue isosurface indicate strong O1...H2–O2 hydrogen bonds between the oxygen of endo-fenchol and water. The weak attractive interactions C–H22...O2 and C–H24...O2 hydrogen bonds involving O_{water}...H_{CH3} are shown in the green iso-surface. These two interactions play an important key role in the stabilisation and the preference of the observed conformer of endo-fenchol...water complex. They are also responsible of alteration in the arrangement of the hydroxyl group induced by the water presence. This study highlights the importance of the weak hydrogen interaction in the stabilisation of the lowest energy conformer.

Conclusions

The pure rotational spectrum of the EF-water complex has been studied using a combination of Fourier transform microwave spectroscopy coupled to a supersonic expansion and theoretical calculation. One conformer has been observed to survive under the supersonic expansion conditions. In order to confirm the structure of the observed conformer multi-isotopic substitution of deuterium was used. The configuration of the observed conformer was unveiled and characterized. The formation of the hydrogen bond with the water molecule alter the arrangement of the hydroxyl group. The conformational change induced by water due to the hydrogen bond interaction

between water and EF was also discussed by performing NBO and NCI analysis. Endo-fenchol acts as proton donor and the presence of weak hydrogen bonds type O_{water}...H_{CH3} were found to be critical in the stabilization of EF...water complex. This study opens the doors to investigate more bicyclic alcohol-water complexes in order to understand the role of the hydrogen bond in the stabilisation of the observed structure. This investigation is also of great interest for the atmospheric chemistry and could be helpful to understand the first step in the process of atmospheric aerosols formation.

Conflicts of interest

There are no conflicts to declare

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