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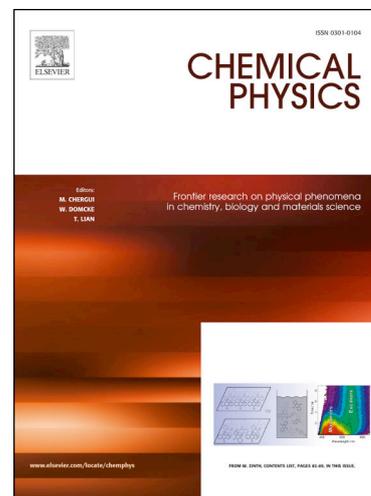
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Gaseous hetero dimers of perfluoro tert-butyl alcohol with hydrogenated alcohols by infrared spectroscopy

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Abstract

Infrared spectroscopy shows that perfluoro tert-butyl alcohol (TBF) forms hydrogen bonded hetero dimers with hydrogenated alcohols (Methanol, 1-butanol and Tert-butanol) in the gas phase at room temperature. DFT calculations confirm these findings providing structures, stabilization energies and allow a first analysis of the ν_{OH} spectra by considering only the diagonal term of the anharmonicity of the vibration. The broad band-shapes of ν_{OH} vibration of the TBF molecule engaged in the heterodimer are discussed, considering vibrational phase relaxation.

Keywords

IR spectroscopy Gas Phase
Perfluoro tert-butyl alcohol - hydrogenated alcohols
H-bonded heterodimers
DFT calculations

1. Introduction

Spectroscopic studies of hydrogen bonded dimers $\text{AH}\cdots\text{B}$ in the gas phase at low pressure is a well-established research field. A central reason is that working under such experimental conditions leads to the determination of intrinsic properties of the dimers, avoiding complications arising from the interactions with the solvent and/or the competing formation of various oligomers in the liquid phase [1-2]. Such an approach allows, directly, the investigation of interactions between the AH and B moieties. Two systems remain as paradigms in this field; namely HCl – dimethyl ether and HCl - acetic acid. The gas phase dimers of these systems have long been thoroughly investigated by vibrational spectroscopy and continue to be scrutinized at a higher level of theory [3-22]. The formation of homo and hetero clusters of alcohols and H-bond donor molecules have been also investigated using a variety of spectroscopic techniques such as cooled in a low temperature matrix, dilution in a solvent, expansion in supersonic slit jets, and also theoretically [12-17,23-69].

This study proposes a new, convenient and easy way to prepare alcohol hetero dimers, thus opening a range of new systems of H-bonding investigations. The main idea is to use perfluoro tert-butanol (TBF) as the H-bond donor, interacting with the oxygen atom of a hydrogenated acceptor. The strategy is based on the strongly acidic character of the TBF molecule ($\text{pK}_a=5.4$) [70] resulting from the electron withdrawing effect of the fluoride substituents, whereas the selected hydrogenated alcohols are comparatively

strongly basic (average pK_a about 16) [71]. It is thus anticipated that the hetero dimer will be $(CF_3)_3COH \cdots OHR$, enabling rationalizing the hetero-dimer as a super triatomic molecule $AH \cdots B$ [20]. The selected hydrogenated molecules are: tert-butyl alcohol $((CH_3)_3COH$, $pK_a = 16.54$ [72] referred here as TBH) with a globular geometry similar to TBF; 1-butanol ($pK_a = 16.1$ [72]) with a linear geometry but the same mass as TBH; and methanol (CH_3OH , $pK_a = 15.5$ [72]) the simplest alcohol with a mass half that of TBH.

This work is also part of a wider project in which we study mixtures of hydrogenated and fluorinated substances; alcohols [73-76] in particular.

2. Experimental conditions

TBH, methanol, 1-butanol and TBF originated from Sigma-Aldrich and Apollo, respectively (purity greater than 99%), as well as CD_3OH and tert-butanol-D9 ($(CD_3)_3COH$ (TBD9) from Eurisotop (purity 98%) were dried using molecular sieves (3 Å). The water content of all the chemicals was measured by Karl-Fisher titration and found to be 400 ppm.

The infrared spectra were measured on a Bruker-Alpha FT-IR spectrometer with a 4 cm^{-1} resolution in the spectral range 400 cm^{-1} to 4000 cm^{-1} after collecting 64 scans. The experiments were performed using a 7 cm path-length gas cell with ZnSe windows, which was purged with argon before each experiment. The sample preparation consisted of boiling a few drops of the desired pure alcohol or mixture inside an argon filled glass flask, followed by adding a few milliliters of this vapour phase (10 Torr) to the spectrometer gas cell using a hypodermic syringe. All the experiments were performed at 298 K.

The DFT calculations were carried out using the program Gaussian09.D01 package [77]. All the structures of homo and hetero oligomers of the hydrogenated alcohols and/or TBF molecules were achieved using the Generalized Gradient Approximation (GGA)-hybrid functional B3LYP with the 6-311+G(2d,p) basis set. The vibrational analysis was performed using the standard Wilson FG matrix formalism based on the harmonic force field approximation [78]. Then, an additional anharmonic vibrational analysis was performed at the same computational level for determining the anharmonicity of the vibrations in monomers and dimers [79]. In the present investigation, we are particularly focussing on the anharmonicity of both ν_{OH} stretching and γ_{OH} torsional

modes of monomers and hetero dimers of hydrogenated alcohols and TBF species. The structural and vibrational calculated properties are gathered in SI (Tables SI-1-4). The calculated energies (electron energy and binding energy) are given in Table SI-1 and the predicted vibrational properties of the ν_{OH} stretching and γ_{OH} torsion modes are gathered in Tables SI-2-3.

3. Experimental results

We will first consider the infrared spectra of the TBF-methanol equimolar binary mixture as representative of the different systems studied here, focusing the attention in the domain of the ν_{OH} vibration (3100-3800 cm^{-1}). The very low pressure gaseous spectra at room temperature of pure TBF, pure methanol and of their mixture are reported in Figure 1. In this spectral domain, the ν_{OH} vibration of monomeric TBF is given by a rather intense and narrow single line centered at about 3632 cm^{-1} having a full width at half-height (FWHH) of about 13 cm^{-1} . A weaker line centered at about 3365 cm^{-1} and having a FWHH of 60 cm^{-1} is also observed; and can be assigned to a negative combination band of the ν_{OH} vibration with the γ_{OH} vibration [23]. We also note that TBF is a very poorly associated liquid [23,35] ruling out any doubt concerning the conclusion that monomeric species are observed here in gas phase at low pressures. In the case of methanol, the infrared spectra displays a single band centered at about 3681 cm^{-1} with a band shape characteristic of the envelop of the ro-vibrational structure encountered in gaseous phase for monomeric alcohols [29,41,62].

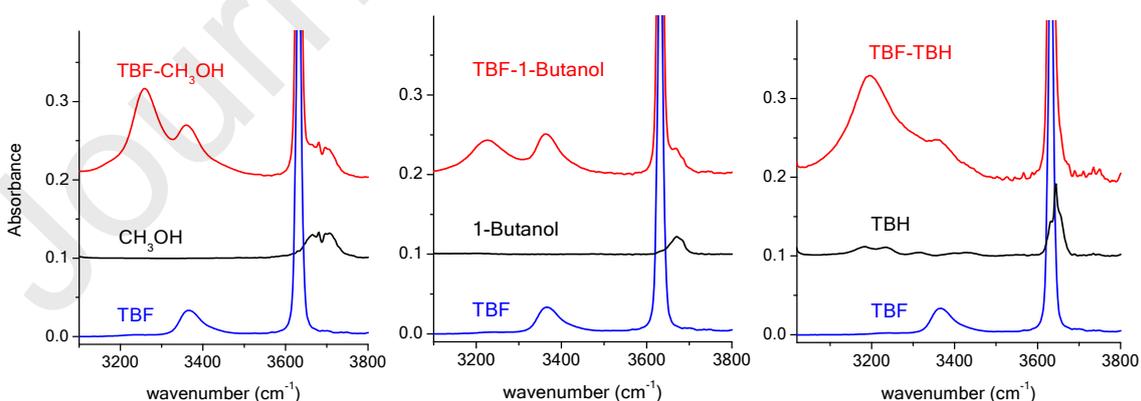


Figure 1. Infrared spectra in the domain of the OH stretching vibration of the gaseous mixtures TBF-CH₃OH, TBF-1-butanol and TBF-TBH compared with the spectra of their pure components.

As for the equimolar mixture of TBF and methanol, two main observations can be made. First of all, a single line is observed at about the frequency of the ν_{OH} vibration of monomeric TBF, but with a slightly broader width (14 cm^{-1}), which superimposes distorting the low frequency side of the band of monomeric methanol. The second observation concerns the emergence *circa* 3258 cm^{-1} of a new broad band (FWHH of about 70 cm^{-1}) inexistent in the two pure alcohols. We also notice that the combination mode reported for pure TBF is slightly affected in the mixture. This band is slightly red-shifted and becomes broader (Table 1).

Table 1. Experimental band center frequencies and Full Widths at Half-Height (cm^{-1}) of the Infrared spectra at room temperature of gaseous phase of equimolar mixtures of TBF with hydrogenated alcohols in the spectral domain of the ν_{OH} stretching vibrations. Anharmonic vibrational transitions and infrared intensities (km/mol) of these vibrations obtained from DFT calculations at the B3LYP/6-311+G(2d,p) computational level.

Species	Experimental				Calculated	
			Combination $\nu_{\text{OH}}-\gamma_{\text{OH}}$		ν	Intensity
	ν	FWHH	ν	FWHH		
Monomers						
TBF	3632	12.8	3365	60	3612.5	83.3
TBH	3643	24			3644.9	11.8
TBD9	3643	26			3644.5	10.3
1-Butanol	3671	38			3670.6	25.6
CH ₃ OH	3681	85			3655.9	26.6
CD ₃ OH	3682	69			3655.9	26.2
Hetero-dimers						
TBF-TBH	3632	15	3363	90	3624.9	23.1
	3197	110			3034.1	641.0
TBF-TBD9	3632	14	3359	100	3627.6	23.2
	3195	120			3042.7	620.3
TBF-1-Butanol	3632	14	3363	76	3652.6	37.1
	3226	98			3041.3	467.7
TBF-CH ₃ OH	3632	14	3360	78	3648.3	42.2
	3258	74			3123.7	892.3
TBF-CD ₃ OH	3632	14	3359	96	3649.3	42.9
	3256	82			3117.8	890.5

We have also performed the same type of measurements on the mixture TBF – deuterated methanol (CD₃OH). The results obtained show that there are almost no differences with the mixture involving hydrogenated methanol (Table 1). Considering

now the TBF-TBH and TBF-1-butanol binary mixtures, we can see on Figure 2 that they present the same trend reported above for the TBF-methanol mixture. We notice that the intense and narrow line, observed in the two mixtures, is approximately centered at the wavenumber of that observed in pure TBF. Again a new broad band is observed in the two mixtures and we also notice that the band center and width of the combination band is slightly affected upon mixing. The spectra of these mixtures and their pure components are displayed in Figure 1.

We have also studied the mixture of TBF with deuterated TBH (TBD9). We found that there was also very slight variation compared to the TBF-TBH mixture (Table 1) as it was found for TBF-deuterated methanol (Figure SI.1). The ensemble of experimental results namely band center frequencies and FWHH measured in all the different systems are reported for comparison in Table 1.

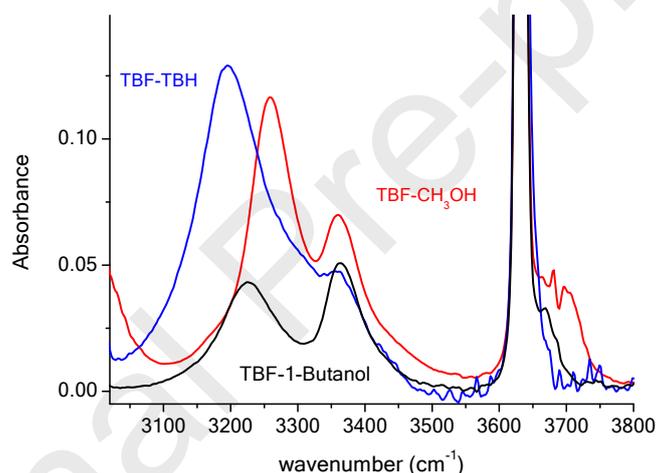


Figure 2. Infrared spectra in the domain of the OH stretching vibration of the gaseous mixtures of TBF with hydrogenated alcohols

From these experimental observations, we can conclude without any ambiguity that the new band observed in all these systems can be assigned to the ν_{OH} vibration of the TBF molecule interacting with the hydrogen alcohol to form a 1:1 heterodimer. More specifically, in all cases, the TBF molecule is the proton donor: the hydrogen atom of its hydroxyl group interacts with the oxygen atom of the hydrogenated alcohol molecule, the acceptor center. This assignment of a $\text{OH}\cdots\text{O}$ hydrogen bond formation is also confirmed by the large red-shift experienced by the ν_{OH} vibration of TBF compared with its value in the monomer molecule.

We also notice that the ν_{OH} vibration of the hydrogenated alcohol molecule (the proton acceptor in the hetero-dimer) corresponding to the terminal hydroxyl group of the H-

bonded alcohol may be superimposed here with the band of the monomers. The frequency of this terminal OH group is so close to that of the non-reacted monomers that the corresponding lines overlap badly and are not resolved.

The comparison of the frequencies of the ν_{OH} vibration of the different heterodimers shows that, although having very close values, nevertheless slightly increase from TBH to 1-Butanol and to methanol. This trend suggests that the strength of the H-bond interaction increases along the sequence Methanol < Butanol < TBH. This is consistent with the pKa values of the different species previously mentioned. Indeed, although the basicity of the three hydrogenated alcohols is not drastically different, thus leading to ν_{OH} vibrations within the same range, the values of the vibration frequencies follow the basicity order. We notice that the broadening (FWHM) of the donor ν_{OH} vibration follows the same order. Moreover the observed trend in both variables (frequency shift and width) appears linear (Figure SI.2). In this context, it is important to mention that we have also studied mixtures of TBH-1-butanol and TBH-methanol, in which the components have very similar basicity. For these mixtures, we have not able to identify any hetero-dimers, a result in marked contrast with those reported here. This clearly reveals the importance of the 'acidic' character of the TBF molecule in the formation of hetero dimers.

To complete the experimental characterization of the different heterodimers, we have resorted to the empirical scale, still widely used in the context of the hydrogen bonding interaction, correlating the shift of the ν_{OH} stretching frequency to the H \cdots O distance in hydrogen bonds. [80-85]. Taking the average value of the ν_{OH} vibration as 3220 cm⁻¹ for the three systems, we found that the OH \cdots O distance is 1.7 Å.

4. Discussion

DFT calculations were performed in order to better characterize the geometry and spectral features of the three hetero dimers. It is found that these entities have rather similar structures involving the proton of the OH hydroxyl group of TBF as the hydrogen bond donor and the oxygen atom of the hydrogenated alcohols as acceptor (Figure 3). These results confirm the experimental inference about the roles played by the TBF and the hydrogenated alcohol molecule in the complex formation. The calculated OH \cdots O distances have been found very close for the three systems with a value of about 1.7 Å. This feature is in perfect agreement with that obtained from the

empirical relationship discussed previously. It was even noticed that the calculated $\text{OH}\cdots\text{O}$ distance is found to decrease slightly according to the sequence Methanol > Butanol > TBH. This trend is in complete agreement with the result concerning the strength of the hydrogen bond interaction discussed in the experimental section.

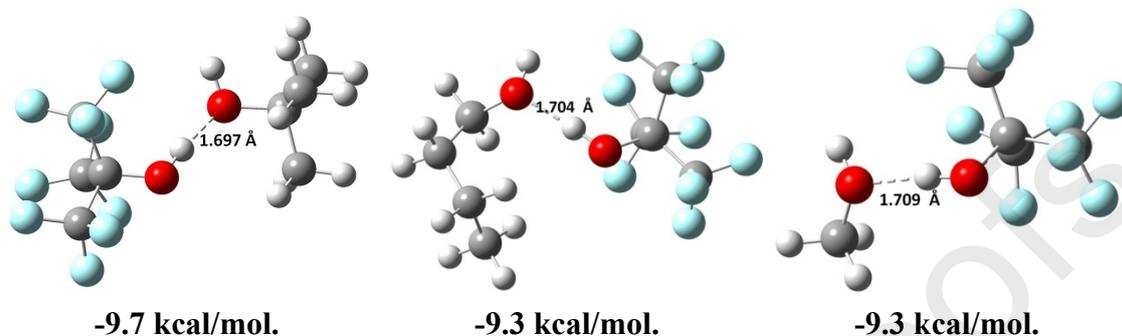


Figure 3. Geometry and binding energy corrected from the BSSE obtained from DFT calculations at the B3LYP/6-311+G(2d,p) computational level for the hetero-dimers in gas phase. From left to right TBF-TBH, TBF-1-Butanol, TBF- CH_3OH .

The calculated stabilization energies of the hetero dimers corrected from the BSSE contribution are found rather similar for the three complexes (Figure 3) and confirm that the TBF-TBH complex is slightly more stable than the two other systems.

Having characterized the structural and energetic aspects of the complex we have tried to analyze comparatively their infrared spectra. Prior to a discussion of the results we would like to make some comments. In the theoretical treatments of the infrared spectra, the complex is considered to be a linear super triatomic molecule $\text{AH}\cdots\text{B}$, for which the high frequency ν_{AH} vibration and the low frequency $\nu_{\text{AH}\cdots\text{B}}$ vibration are coupled by an anharmonic potential [3,4,11,12,19,22,86-92]. Vibrational transitions from different levels of the low-frequency oscillator in the $\nu_{\text{AH}}=0$ state to different low-frequency levels in the $\nu_{\text{AH}}=1$ state with a shifted origin of the potential result in a progression of lines which for moderate displacements is centered at the pure AH stretching transition and displays a mutual line separation by one quantum of the low frequency mode (the so-called Franck-Condon type progression in the literature). An examination of the band-shape of the spectra of the dimers of the systems reported here does not show any type of such progression. The band of the dimer appears to be unique. However, as will be addressed later (as to the physical origin of the profile), we may wonder whether, in this band, there are some faint contributions which may be assigned to combination modes of the ν_{OH} transition with rocking modes of CF_3 groups. It seems that in the region of interest the only effect of the H bond interaction is to slightly broaden the

negative combination existing between the OH stretching vibration and the low frequency OH torsion (Table 1). Therefore, in a first approach, we will admit as a working hypothesis that the band of the complex is a single one and not a superimposition of the Franck-Condon type progression mentioned previously.

On the basis of this hypothesis, we have resorted to DFT calculations considering only the anharmonicity of the ν_{OH} vibration and neglected any possible coupling with a lower vibration. We must also emphasize that a deeper treatment considering the interaction of the modes based upon the calculation of the full potential energy surface (PES) will be too demanding, from the point of view of computer resources, for the rather big molecules considered here.

We have first of all calculated for TBF and the hydrogenated monomers the frequency of the ν_{OH} vibration and found a nice agreement with the experimental values (Table 1). We have then calculated the values of the ν_{OH} vibrations of the terminal OH group of the dimers and the ν_{OH} vibration of the hydroxyl group of TBF as an H bond donor (Table 1). The calculated frequencies of the terminal OH values overestimate the experimental values (about 0.2-0.4%) whereas the contrary is observed for the ν_{OH} vibration of the hydroxyl group in the complex (about 3-6%). Therefore we should admit that the agreement obtained between calculations and experimental results can be only considered as fair. However, we note that the calculated frequencies values show that the strength of the H-bond interaction increases according to the trend already reported, i.e., Methanol < Butanol < TBH. In view of the working hypothesis, this result which is consistent with the experimental observation can be considered as rather satisfying. A better numerical agreement certainly will rely on considering not only diagonal anharmonic coefficient but also the non-diagonal coefficients as has been underlined in recent studies [22,65,91,92].

The last point which merits to be discussed concerns the origin of the large broadening (circa 100 cm^{-1}) of the heterodimer band shape (Table 1). Such large broadening is again a signature of H-bond. In the liquid state, this broadening generally results from the modulation of the interatomic $\text{OH}\cdots\text{O}$ vibration due to the interaction with the thermal bath leading in turn to the broadening of the coupled ν_{OH} high frequency vibration [93]. This mechanism cannot be considered here due to the lack of thermal bath. Under the thermodynamic conditions of the gas phase experiment performed here only collisions between molecules are possible. The corresponding mean time between

collisions being in the nanosecond time scale this cannot explain the sub-picosecond scale corresponding to the large broadening observed.

Therefore, we will try to discuss the observed broadening on the bandshape of the ν_{OH} profile of the TBF donor molecule on the ground of physical considerations.

The shape of the infrared profile results from the convolution of a vibrational profile by a rotational one if the vibrational and reorientational dynamics are independent [12,94,95]. However, we can discard the importance of the rotational contribution in the bandshape of the ν_{OH} profile of the TBF H-bond donor molecule according to the following line of reasoning. In gas phase, at the low pressure of the experiment (a few Hg mm), the molecule is freely rotating. Considering the TBF monomer, we found that the ν_{OH} profile is given by a single line having a broadening of about 10 cm^{-1} after correction of the finite effect of the resolution (Figure SI.3). Let us assume that this profile is only the envelope of the rotational structure and that the vibrational contribution is negligible. When the TBF molecule is engaged in a complex, the rotational contribution would be strongly hindered and its contribution in the infrared profile would be much smaller than that of the freely rotating molecule. The broadening of the ν_{OH} profile of TBF in the complex is about 100 cm^{-1} and therefore much greater than that due to the rotational contribution, which should be less than 10 cm^{-1} . Thus, we can safely infer that the shape and broadening of the ν_{OH} profile of TBF in the complex mostly provides information on the vibrational phase relaxation.

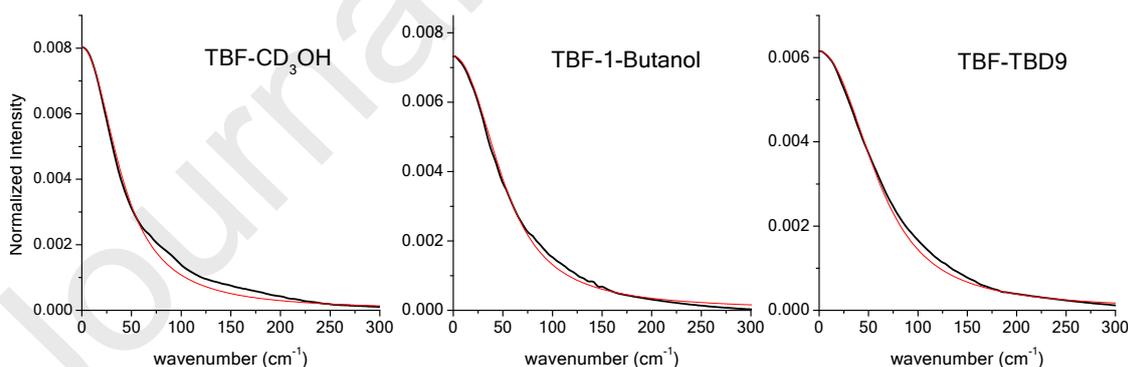


Figure 4. Comparison of the experimental symmetrized band-shapes (see text) of the OH stretching vibration of the mixtures (black) with that calculated using the Voigt profile (red).

We have checked that the ν_{OH} profile of the TBF donor molecules engaged in the heterodimers is neither Gaussian nor Lorentzian, but they could be nicely described by a Voigt profile which results from the convolution of a Gaussian by a Lorentzian. This is

illustrated on Figure 4. Interestingly, we found that the contributions to the width of the experimental bandshapes by the Gaussian and Lorentzian profiles are of the same order of magnitude (Table SI.5). Such a result suggests that the inhomogeneous and the homogeneous contributions associated to Gaussian and Lorentzian profiles, respectively, are both present in the experimental bandshapes. However, such simple analysis does not seriously allow disentangling the relative importance of the two processes in the bandshape, but merely indicate that both processes may be involved in the vibrational relaxation mechanism. We may speculate that the inhomogeneous contribution corresponds to a broad continuous distribution of different ν_{OH} transition frequencies reflecting a rather-continuous variation of hydrogen bonds configurations. The origin of the homogeneous contribution is more difficult to assess but the corresponding line-width could be associated with rapid variations in the angle and length of the local $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds [96]. We may also suspect that the homogeneous contribution is correlated with intra-molecular vibrations due to anharmonic coupling. A support to this statement may be suggested by the fact that the combination of the OH torsion with the ν_{OH} mode existing in pure TBF is affected (and in particular its width, see Table 1) upon mixing with the hydrogenated alcohol. However, in the absence of more information and calculations aimed at studying the effects of the diagonal and non-diagonal anharmonicity terms, a deep interpretation of the homogeneous contribution remains speculative.

5. Conclusion

We have shown that fluoro tert-butyl alcohol (TBF) can form easily complex in the gas phase at RT with a variety of hydrogenated alcohols such as methanol, butanol, tert-butanol and some of their deuterated derivatives. In all these systems, it is found that the molecules interact via the formation of an $\text{OH}\cdots\text{O}$ hydrogen bond between the proton of the hydroxyl group of the fluorinated molecule, playing the role of H-bond donor, with the oxygen atom of the hydroxyl group of the hydrogenated alcohol as acceptor. This conclusion is reached from the observation in the ν_{OH} region of the infrared spectra of a new band in the TBF-hydrogenated alcohol mixtures. This band is not detected in the spectra of the separate alcohols, and presents the signatures of H-bonding (i.e., a strong red-shift of the band from those of the monomers, a relatively strong intensity and a large broadening). It is inferred on the basis of the red shift values and using empirical

relation used in H-bond investigations to specify the O-H \cdots O intermolecular distance that the strength of the H-bond interaction, although not very different, increases in the three hetero dimers according to the sequence TBH > 1-Butanol > Methanol. DFT calculations confirm the formation of these hetero-dimers by specifying their structure and energy of formation. These calculations have been also aimed at studying the infrared spectra of the ν_{OH} stretching band. Considering only the diagonal anharmonic coefficient of the OH vibration, the calculations are found in a remarkable agreement with those measured for the monomers species. However, they only give the correct trend experimentally observed for the values of the ν_{OH} band of TBF in the dimer, but without good numerical agreement. This shows that, in the domain of hydrogen bonding, the need to take into account the non-diagonal anharmonicity term is important. Finally, the profile of the ν_{OH} stretching band of the H bond donor TBF was analyzed using a Voigt profile. This approach suggests that two processes would contribute to the broadening. An inhomogeneous contribution resulting from the distribution of the ν_{OH} transition frequencies, reflecting a rather continuous variation of hydrogen bond configurations, and a homogeneous contribution, which is likely associated with rapid variations in the angle and length of the local O-H \cdots O hydrogen bond and may be correlated with intra-molecular vibrations due to anharmonic coupling.

In conclusion, we guess that the systems here studied could be also considered as model systems in the domain of hydrogen bonding. And as such they merit a deeper examination. The bands are rather unique, apparently, and without the complication of sub-structure and therefore might be of interest for comparison with the deep analytical theories [14,22]. Similarly, the role of non-diagonal anharmonicity, which is a research field of current interest, has been only explored as far as we know on pure alcohol clusters. In this context, the studies of hetero alcoholic clusters would certainly enable an interesting extension [65,90]. Finally, we believe that these systems merit to be tackled with time-resolved spectroscopy [97-99].

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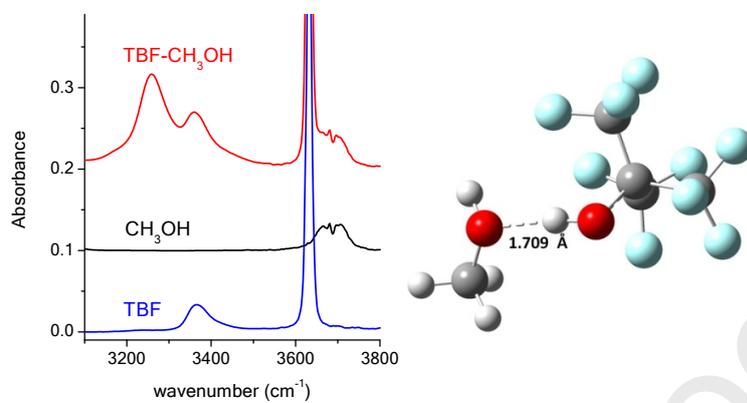
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Declaration of interests

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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:



Highlights

- * H-bonded heterodimers of perfluoro tert-butanol with hydrogenated alcohols
- * IR spectroscopy in gas phase
- * Inhomogeneous and homogeneous vibrational contributions
- * DFT Calculations