

Influence of environment and association with water, to internal structure of trifluoroacetylacetone. Matrix isolation FTIR study

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The structure of trifluoroacetylacetone in argon and nitrogen matrices and association with water molecules were studied by the means of Fourier transform infrared absorption spectroscopy (FTIR) aided with density functional theory (DFT) calculations. The absorption bands of trifluoroacetylacetone isolated in argon can be attributed to the single conformer 1,1,1-trifluoro-4-hydroxy-3-penten-2-one (AcAcF₃(CO)) which is in good agreement with previous studies. Absorption bands of trifluoroacetylacetone isolated in nitrogen matrix cannot be explained by the presence of only one conformer and with the aid of DFT calculations both conformers 1,1,1-trifluoro-4-hydroxy-3-penten-2-one and 5,5,5-trifluoro-4-hydroxy-3-penten-2-one (AcAcF₃(OH)) are confirmed to coexist in the nitrogen matrix. Addition of water to the trifluoroacetylacetone–matrix mixture resulted in appearance of new spectral bands not belonging either to trifluoroacetylacetone or water monomers confirming the formation of trifluoroacetylacetone–water complexes. The most abundant isomer out of trifluoroacetylacetone–water complexes was found to be the one formed from 5,5,5-trifluoro-4-hydroxy-3-penten-2-one and water attached to its C=O group in both matrices, the other one isomer of 1,1,1-trifluoro-4-hydroxy-3-penten-2-one–water complex is also observed in smaller amounts.

Keywords: matrix isolation, water complexes, acetylacetone, trifluoroacetylacetone.

1. Introduction

Hydrogen bonding is an important interaction that governs many different biological and chemical processes in nature. It determines molecular structure and dynamics in both organic and inorganic compounds [1,2]. Hydrogen bonds can be formed both inside a molecule and between molecules. One of the most commonly occurring cases are water clusters or water-organic molecule complexes. Hydrogen bond can differ in strength depending on the molecule and its environment. A special case of hydrogen bond — resonance assisted hydrogen bond (RAHB) is observed in molecules with resonant structures where electron conjugation favors proton transfer from donor towards acceptor [3]. In most of the cases RAHB is stronger than normal hydrogen bond [3].

One of the simplest molecules where RAHB is present is acetylacetone (noted hereafter as AcAc). Its enol

(Z-4-hydroxy-3-penten-2-one) form is stabilized by the internal hydrogen bond and is dominant in gas phase while the keto form exists in smaller concentrations in gas and liquid phases and for molecules isolated in the low-temperature cryogenic matrices. The keto concentration in solutions increases together with solvent polarity [4–7]. The structure and symmetry of acetylacetone molecule has been thoroughly analyzed [7–13]. The conclusion most of the theoretical and experimental methods come to is that the two resonant forms (Fig. 1) of acetylacetone have C_s symmetry with hydrogen localized near one of the oxygen atoms and π electrons partially delocalized in the chelated ring [7]. Proton tunneling between two stable sites near oxygen takes place. The tunneling is highly coupled with two another large amplitude motions in acetylacetone, namely CH₃ torsional vibrations [14]. In the experimental spectra tunneling effects results in OH stretching mode being too broad to be observable and out of plane and in-plane OH deformation

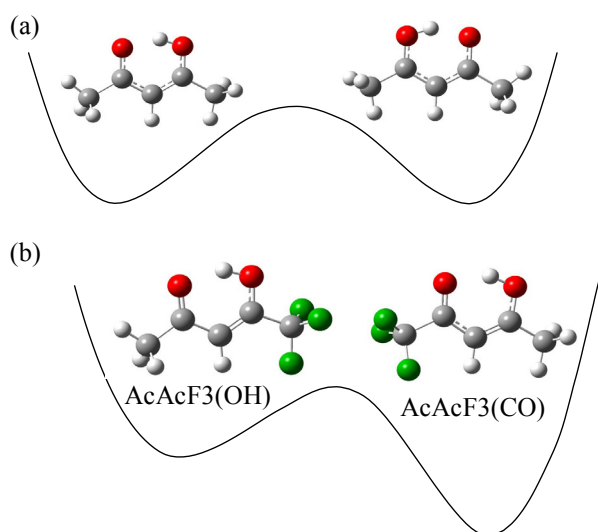


Fig. 1. (Color online) Acetylacetone (a) and trifluoroacetylacetone (b) molecules with their potential function for the hydrogen tunneling coordinate.

modes are also affected in some degree [14–16]. Isotopically modified [17] and halogenated [18–22] derivatives of AcAc have also been extensively studied using experimental and theoretical methods. One of the particularly interesting cases from halogenated derivatives is trifluoroacetylacetone (noted hereafter as AcAcF3). The major difference of this molecule compared to the parent AcAc molecule is the broken symmetry of the ring by CF₃ group replacing CH₃ group (see Fig. 1). This results that potential energy surface for the hydrogen tunneling coordinate becomes asymmetric with the two energy wells of different depth. AcAcF3 has been studied by experimental and theoretical methods but to a lesser extent compared to its parent molecule, acetylacetone [19,21–23].

The system becomes even more complicated if we add to the system water molecule with the ability to form intermolecular hydrogen bond. There are two recent studies of acetylacetone–water and hexafluoroacetylacetone (AcAcF6)–water complexes [24,25]. Both of these studies predict single stable AcAc–water and AcAcF6–water complexes. In both systems water is bound to AcAc C=O group, but water orientation in the respect of AcAc and AcAcF6 is different [24]. The broken symmetry of AcAcF3 molecule opens more possibilities for the formation of AcAcF3–water complexes therefore the identification of the possible AcAcF3–water complexes from experimental data is important.

In this study we present matrix isolation study of AcAcF3 isolated in argon and nitrogen matrices in order to estimate the influence of more interacting with the trapped molecule nitrogen environment to the formation of possible structures of AcAcF3. In addition we performed studies with AcAcF3–water mixtures in order to determine the possibility for water and AcAcF3 to form intermolecular hydrogen bond, and possible geometries and stability of formed

hydrogen bond complexes. The obtained results are compared with the similar studies of acetylacetone and hexafluoroacetylacetone [24,25].

2. Methods

2.1. Experimental

Acetylacetone (99%), trifluoroacetylacetone (98%) and hexafluoroacetylacetone (99%) from Sigma-Aldrich and distilled water were degassed in the vacuum system by using freeze pump thaw cycle and used without further purification. Nitrogen (99.999%), argon (99.999%) gases from Elme Messer Gaas were used without additional treatment.

Sample and matrix gas mixtures were prepared in the glass vacuum system. Sample to matrix gas ratios were estimated by measuring partial gas pressure in the vacuum system with typical pressure of 1 mbar for the sample molecule and 500 mbar for the matrix gas. Trifluoroacetylacetone and water ratios were varied in a wider range (AcAcF3:water from 1:0.5 to 1:4) in order to obtain spectra with different amounts and sizes of molecular complexes. In a typical experiment approximately 20 mmol of gas mixture was deposited in 90 minutes onto a spectral window (cesium iodide) held at 10 K in a closed cycle He cryostat (Leybold-Heraeus RW2).

Infrared absorption spectra were recorded in the 500–4000 cm⁻¹ range using a Bruker IFS 120 spectrometer at 0.5 cm⁻¹ resolution. The background spectra and the sample spectra were measured under the same conditions, averaging 256 spectra. A controlled warming of the matrix was performed to induce complex formation. The spectra were recorded at 10, 20, 25 and 30 K temperatures. After, the sample was cooled down back to 10 K and additional spectrum was recorded.

2.2. Calculations

Density functional theory (DFT) at the B3LYP/6-311++G(3df,3dp) level [26] was used to optimize the geometries and calculate harmonic frequencies of single AcAc, AcAcF3 and AcAcF6 molecules and their complexes with one water molecule. All calculations were performed using Gaussian 09 program package [27]. In a typical calculation nosymm keyword was used in order to ensure that calculation program does not enforce symmetry for the AcAc and AcAcF6 molecules. This was found to be very important in the calculations of AcAc, as potential minimum for the torsional rotation of CH₃ groups is very shallow. The calculated wavenumbers in tables and figures presented without scaling factor, except Figs. 5 and 7 where calculated OH stretching wavenumbers are presented scaled (scaling factor 0.96) for more convenient comparison with experimental data. The scaling factor was chosen to give best fit for already identified AcAc–water OH stretch bands of water bound to AcAc [24,25].

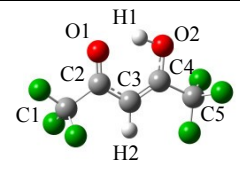
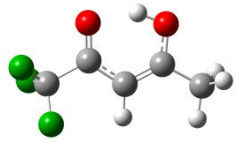
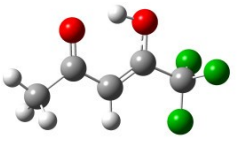
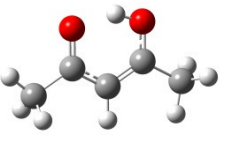
3. Results

3.1. Quantum chemistry calculations

Calculations were performed for single acetylacetone molecule and its fluorinated derivatives to evaluate hydrogen bond strength changes upon fluorination of the molecule.

The most straightforward parameters to evaluate hydrogen bond strength are O–H···O distance and wavenumbers of OH vibrational modes. The optimized geometric parameters are presented in Table 1, along with the calculated energy difference for two lowest energy trifluoroacetylacetone isomers and out-of-plane OH vibrational mode values.

Table 1. B3LYP/6–311++G(3df,3dp) calculated parameters: electronic energy E , ΔE is the energy difference between AcAcF3(CO) and AcAcF3(OH) isomers ($E_{\text{AcAcF3(OH)}} - E_{\text{AcAcF3(CO)}}$), geometric parameters (bond lengths and angles), γ_{OH} vibrational mode wavenumber and delocalization coordinate (see text)

Parameter	AcAcF6	AcAcF3(CO)	AcAcF3(OH)	AcAc
				
E , a.u.	–941.58830	–643.76592	–643.76385 $\Delta E = 5.4$ kJ/mol	–345.93706
$d_{\text{O1}\cdots\text{H1}}$, Å	1.70	1.66	1.63	1.61
$d_{\text{O2}\cdots\text{H1}}$, Å	0.99	1.00	1.00	1.00
$d_{\text{O1}\cdots\text{O2}}$, Å	2.58	2.56	2.53	2.53
angle O1···H1–O2, deg	144.6	147.4	147.4	149.2
γ_{OH} , cm^{-1}	906.4	964.6	972.1	1010.1
$d_{\text{C2}=\text{O1}}$, Å	1.22	1.23	1.24	1.24
$d_{\text{C3}=\text{C4}}$, Å	1.35	1.37	1.35	1.37
$d_{\text{C4}-\text{O2}}$, Å	1.31	1.32	1.32	1.32
$d_{\text{C2}-\text{C3}}$, Å	1.43	1.42	1.45	1.44
Q	0.167	0.132	0.17	0.15

Atom substitution can affect molecular structure and dynamics in two ways: i) steric effect due to different atom sizes or ii) changed charge distribution if the substitute atom is more or less electronegative than the original one. Since fluorine is both bigger and much more electronegative (electro-attractive) than hydrogen, it is important to evaluate the possibility of both effects. The steric effect would result in big fluorine atoms pushing the O–H and C=O groups closer together and thus shortening the O–H···O distance and strengthening internal hydrogen bond. However, our calculation results indicate that O–H···O distance increases, indicating a weakening of the hydrogen bond with the addition of fluorine atoms. This result allows to conclude that steric effect is less significant than the changes in charge distribution induced by higher fluorine electronegativity compared to the hydrogen. Another important parameter influencing the stability of the molecule and often used as the indicator of the internal hydrogen bond is the π electrons delocalization. It can be evaluated from the interatomic distances in the chelated ring. The stronger the delocalization, the smaller the difference between double and single bonds. This difference can be expressed through parameter $Q = d_{\text{(C-O)}} - d_{\text{(C-O)}} + d_{\text{(C-C)}} - d_{\text{(C=C)}}$ known as the coordi-

nate of π bond delocalization [18,28]. According to this parameter, the strongest delocalization is observed for AcAcF3(CO), the weakest for AcAcF3(OH) with AcAc and AcAcF6 in between. It is interesting to note that O···O distance and spectroscopic (wavenumbers of stretch and deformation vibrations of OH group) parameters indicates stronger hydrogen bond in AcAcF3(OH) than in AcAcF3(CO), but AcAcF3(CO) has much higher π electron delocalization. The calculations also predicts that the total electronic energy is lower for AcAcF3(CO) by 5.4 kJ/mol. The higher π electron delocalization in AcAcF3(CO) is one of the important parameters stabilizing this configuration. However based on current observation it seems that π electron delocalization is not a good parameter for the evaluation of internal hydrogen bond strength, but it is more associated with the stability of the whole molecule. This observation agrees well with the previous theoretical study of this system [22].

Calculated energy of AcAcF3 (CO) is lower by 5.4 kJ/mol compared with AcAcF3(OH) which, according to Boltzmann distribution, would correspond to 89% AcAcF3(CO) and 11% AcAcF3(OH) mixture at room temperature. In our experimental conditions we have calculated for the

strongest absorption bands the signal to noise ratio of 300:1 thus observing both AcAcF3(CO) and AcAcF3(OH) is plausible.

Several possible structures for acetylacetone and water complexes were evaluated in the previous studies [24,25]. The same procedure has been performed for AcAcF3 in this study. The potential energy surface of the AcAcF3–water system is more complicated by the presence of CF₃ group and the possibility of hydrogen atom tunneling changing molecule configuration from one isomer to another. Out of all possible AcAc groups to attract water molecule (oxygen atoms from C=O group and from C–O–H group, as well as fluorine from CF₃), the most stable complex geometry is found with water molecule near the C=O group in acetylacetone and all its fluorinated derivatives. This can be explained by strong electropositive effect of C=O group of AcAc molecules originating from lone pair electrons in oxygen sp^2 configuration. The only change is the rotation of water molecule with respect to AcAc depending whether oxygen in water is feeling repulsion or attraction to CF₃ or CH₃ groups, respectively. The next closest isomer of AcAcF3–water is the AcAcF3(CO) isomer with water bonded on OH side of the AcAcF3 molecule. This isomer is 2 kJ/mol higher in energy than the corresponding AcAcF3(CO) with water on C=O side. The isomers with this energy difference could be expected to be seen in experimental spectra, but in corresponding systems of AcAc and AcAcF6 we [25] and authors of Ref. 24 have never observed the water molecule on the OH side of the acetylacetone molecule. Experimental spectra, as it will be discussed in experimental section also does not suggest the appearance of more than two species, therefore we did not include this isomer in the discussion. All other possible

configurations are more than 10 kJ/mol higher in energy and we do not expect to observe such isomers in experimental spectra.

Intermolecular hydrogen bond strengths in different AcAc derivative complexes with water can be compared using geometric parameter of the complex — distance between oxygen in acetylacetone and hydrogen in water that forms the bond. Unlike with single AcAc molecules, for the complex we can also evaluate intermolecular hydrogen bond strength from calculated and experimental bound OH stretching modes in water molecule. The complex formation energy (calculated by subtracting the energies of separate molecules from the energy of the associate) is also used in determining the stability of the complex.

The calculated energy differences, interatomic distances and water bound OH stretching mode frequencies are presented in Table 2. The trend of intermolecular hydrogen bond strength is the same as for internal hydrogen bond strength in the single acetylacetone and its fluorinated derivative molecules. The strongest hydrogen bond is for AcAc–H₂O, the weakest — for AcAcF6–H₂O complex. Clearly, the changed charge distributions play an important role. In the case of AcAcF6–water and AcAcF3(CO)–water complexes, repulsion between oxygen in water molecule and CF₃ group fluorine atoms in the fluorinated AcAc molecule causes the increase of the intermolecular distance (see distance $d_{O1...Hw}$ in Table 2) compared to not fluorinated AcAc. The possible attraction between hydrogen atoms in H₂O and fluorine atoms in CF₃ groups is not strong enough to compensate this repulsion as the interatomic distances are too large (equal or larger than 3 Å). There is also some repulsion effect between the hydrogen atoms in water and in C–OH group of acetylacetone.

Table 2. B3LYP/6–311++G(3df,3dp) calculated: complex binding energies E_B^* , ΔE^{**} is the energy difference of AcAcF3(CO)–water and AcAcF3(OH)–water isomers, optimized bond lengths between atoms involved in hydrogen bond and wavenumbers of vibrational modes H₂O $\nu_{OH_{bound}}$ and AcAc γ_{OH}

Parameter	AcAcF6 + H ₂ O	AcAcF3(CO) + H ₂ O	AcAcF3(OH) + H ₂ O	AcAc + H ₂ O
E_B^* , kJ/mol	11.5	15.3	20.1	23.5
ΔE^{**} , kJ/mol	—	0	0.7	—
$d_{O1...H1}$, Å	1.73	1.68	1.65	1.63
$d_{O2...H1}$, Å	1.00	0.99	1.00	1.00
$d_{O1...Hw}$, Å	2.07	2.03	1.96	1.91
H ₂ O $\nu_{OH_{bound}}$, cm ⁻¹	3779.4	3754.5	3691.6	3640.8
AcAc γ_{OH} , cm ⁻¹	884.2	943.6	941.3	987.4

Notes: * Complex binding energy E_B is calculated by subtracting energies of complex forming monomer molecules from the energy of complex, e.g., for AcAc water complex ($E_B = E_{complex} - E_{water\ monomer} - E_{AcAc\ monomer}$),

** $\Delta E = (E_{AcAcF3(CO)+H2O} - E_{AcAcF3(OH)+H2O})$.

The internal hydrogen bond is weakened by the addition of water as the same oxygen atom now serves as an acceptor of two hydrogen bonds. Theoretical calculations confirm this as the distance between the oxygen of C=O group and hydrogen of C–OH group in acetylacetone (denoted as $d_{O1...H1}$ in Tables 1 and 2) increases after addition of water. The values of interatomic distances also confirm that the trend of internal bond strength remains the same, with AcAc exhibiting the strongest and AcAc6F the weakest bond. Another proof that in acetylacetone–water associates, AcAc and its derivatives exhibit a weaker internal hydrogen bond than the pure molecules is the decrease in calculated γ OH frequency.

3.2. Experimental results

3.2.1. Acetylacetone and fluorinated acetylacetone molecules isolated in argon and nitrogen matrices

Acetylacetone and fluorinated acetylacetone (AcAcF3 and AcAcF6) molecules isolated in argon and nitrogen

matrices were studied in order to qualitatively evaluate fluorination effect on infrared absorption spectrum and possible isomer structure of these molecules. All three molecules have OH stretch band that is highly red shifted (based on DFT calculations) and broadened due to the strong internal hydrogen bond. The band broadness does not allow to unambiguously distinguish this band from background in experimental spectra. B3LYP calculations predict four bands in the wavenumber region corresponding to CH₃ stretching vibrations for AcAcF3 molecule (see Table 3). Three of them have very low intensity and one, corresponding to coupled ν CH₃/ ν OH mode, is only slightly more intense. Experimentally, we observe these four bands to be very weak. This is in good agreement with previous experimental observations [19,21].

Table 3. Experimental wavenumbers of AcAcF3 in argon and nitrogen matrices compared to calculated wavenumbers of AcAcF3(CO) and AcAcF3(OH)

Experimental			Calculations					
Ar	N ₂	Ar*	AcAcF3 (CO)			AcAcF3 (OH)		
$\tilde{\nu}$, cm ⁻¹	$\tilde{\nu}$, cm ⁻¹	$\tilde{\nu}$, cm ⁻¹	Mode	$\tilde{\nu}$, cm ⁻¹	Int.	Mode	cm ⁻¹	Int.
3110 (vw, br) 3125 (vw, br)	3120 (vw, br)		ν CH	3246.5	2			
						ν CH	3241.0	1
						ν CH ₃	3149.0	10
3018.7 (w)	3018.7 (w)		ν OH/ ν CH ₃	3147.3	31			
			ν OH	3134.2	236			
2978.0 (w)	2978.0 (w) 2964.0 (w)		ν_a CH ₃	3094.3	2			
						ν_a CH ₃	3088.6	4
						(ν OH/ ν_s CH ₃) _s	3036.5	101
2932.5 (w)	2932.5 (w)		ν_s CH ₃	3041.5	1			
						(ν OH/ ν_s CH ₃) _a	3030.5	250
	1664.4 (m)					ν C=C/ ν C=O	1700.2	273
1647.0 (w, br)	1647.0 (w)	1646 (w)	ν C=O/ ν C=C	1687.5	160			
						δ OH/ ν C–C=C	1651.6	136
1609.3 (s)	1607.6 (s)	1608 (s)	δ OH/ ν C–C=C	1640.2	500			
1473.0 (w)	1473.0 (w)	1472 (w)	δ OH/ δ CH/um CH ₃	1496.9	35			
						tw CH ₃	1474.4	9
		1436 (w)	tw CH ₃	1471.7	9			
						δ OH/ δ CH/ um CH ₃	1470.2	12
1424.3 (m)	1424.3 (m)		δ OH/um CH ₃	1464.6	105			
						δ CH/um CH ₃	1463.2	47
		1378 (w)	um CH ₃	1418.4	15			
						δ OH/um CH ₃	1401.0	93

1364.0 (w)	1364.0 (m)	1363 (w)	$\delta\text{OH}/\text{um CH}_3$	1388.7	99			
						$\delta\text{OH}/\delta\text{CH}/\text{um CH}_3$	1386.5	63
1300.8 (m)	1301.5 (m)	1274 (w)	δOH	1303.7	156			
1290.0 (m, br)	1290.7 (s)							
1273.5 (m)	1275.3 (m)							
						$\delta\text{OH}/\delta\text{CH}/\nu\text{CF}_3$	1295.3	513
1212.9 (s)	1212.2 (m)	1208 (s)	$\delta\text{OH}/\delta\text{CH}$	1220.3	124	$\delta\text{CH}/\rho\text{CH}_3/\nu\text{CF}_3$	1228.5	64
1207.7 (s)								
1199.8 (s)								
						νCF_3	1181.7	286
						νCF_3	1153.8	279
1175.9 (s)	1172.6 (s)	1176 (s)	$\delta\text{CH}/\nu\text{CF}_3$	1142.0	249			
1166.5 (s)								
1156.6 (s)								
						δCH	1131.0	74
1110.2 (vs)	1110.2 (s)	1100 (vs)	δCH	1125.0	211			
1035.7 (vw)	1035.7 (vw)	1036 (w)						
			tw CH_3	1060.9	1	tw CH_3	1048.7	3
1009.0 (vw)	1009.0 (w)	1009 (w)	ρCH_3	1029.7	7			
	987.8 (w)					ρCH_3	1000.3	17
944.3 (w)	943.2 (w)	945 (w)						
910.1 (w,br)	897.8 (w)	934 (w)	γOH	964.6	66	γOH	972.1	55
	886.8 (vw)							
	878.6 (vw)							
			$\Delta (\delta\text{C}=\text{C}-\text{OH})$	961.4	4			
						$\Delta (\delta = \text{C}-\text{C}=\text{O})/\rho\text{CH}_3$	935.1	12
862.0 (m)	862.0 (m)	862 (m)	$\nu\text{C}-\text{CH}_3/\nu\text{C}-\text{CF}_3$	867.4	39			
	846.0 (vw)							
	802.6 (m)					$\gamma\text{CH}/\rho\text{CH}_3$	828.9	40
791.2 (m)	792.5 (m)	791 (m)	γCH	817.0	40			
761.7 (w)	761.6 (w)	762 (w)	γCH	775.3	1			
						$\Gamma (\gamma\text{C}=\text{C}-\text{OH})$	737.1	2
729.7 (m)	729.7 (m)	730 (m)	um CF_3	729.2	30			
	720.1 (w)					$\Delta/\text{um CF}_3$	721.8	11
						$\Gamma/\text{tw CH}_3$	608.9	0.005
668.9 (vw)			tw CH_3	600.1	1			
	574.9 (s)							

Notes: Ref. 21, br — broad, vs — very strong, s — strong, m — medium, w — weak, vw — very weak, ν — stretching, δ — in-plane deformation, γ — out of plane deformation, ρ — rocking, tw — twisting, um — umbrella, Δ — whole molecule in-plane deformation, Γ — whole molecule out-of-plane deformation vibrations.

The most intense bands in the experimental spectrum of acetylacetone isolated in argon matrix are the bands in the 1700–1600 cm^{-1} region (Fig. 2). These broad bands are assigned to highly coupled C=C and C=O stretching vibrations. The spectrum of AcAcF6 in the same region contains two low-intensity doublet bands.

The spectrum of AcAcF3 consists of one strong and a number of low-intensity bands. The band broadening can be associated with strength of internal hydrogen bond. The strongest one among the three structures according to DFT calculations is in AcAc. In this molecule the bands involving OH movement are the broadest ones. On the contrary,

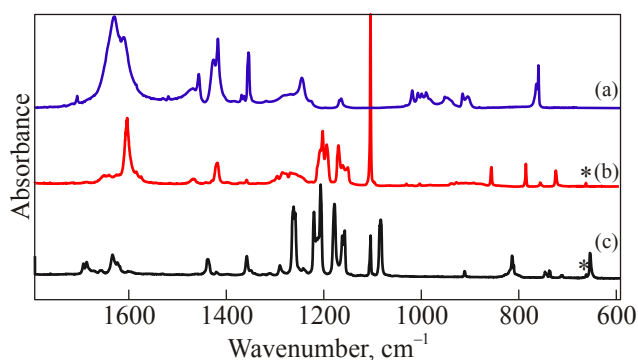


Fig. 2. Infrared absorption spectra of AcAc (a), AcAcF3 (b) and AcAcF6 (c) isolated in argon matrix at 10 K, sample to matrix ratio 1:500, * denotes incompletely compensated atmospheric CO₂ absorption.

AcAcF6 has the weakest internal hydrogen bond, and the bands are narrowest out of the three structures, with the exception of the band corresponding to γ OH vibration.

In the region from 1500 to 1300 cm⁻¹ several spectral bands associated with in-plane deformational OH vibration coupled with methyl group vibrations are observed (see Fig. 2). This is why this region so strongly changes upon fluorination. The most intense peak assigned to deformational OH vibration is observed at 1270 cm⁻¹. It is broad and has internal structure in the spectra of AcAc and AcAcF3, but is much narrower and well defined in the case of AcAcF6. For AcAcF3 and AcAcF6, the stretching vibrations in CF₃ group combined with ring deformations (and especially OH and CH deformational modes) are present as complicated doublets at 1200 cm⁻¹.

High-intensity narrow peak at 1110 cm⁻¹ is observed for AcAcF3. The peak at the same position but with much lower intensity is also observed for AcAcF6. This band based on DFT calculations and comparison of AcAcF3 and AcAcF6 molecules was assigned to in-plane CH bending of olefinic carbon. It is interesting to note that this band is red shifted from AcAc (1171 cm⁻¹) by 60 cm⁻¹ for both fluorinated structures.

Calculations in the spectral range between 1000–700 cm⁻¹ predicts 4 medium strength bands for AcAcF3(CO) isomer (see Table 3): umbrella CF₃ (calculated at 729 cm⁻¹); CH out of plane deformation (817 cm⁻¹); ring deformation together with antisymmetric C–C stretch of terminal (C1–C2 and C4–C5 bonds) groups (867 cm⁻¹); and OH out of plane deformation (964 cm⁻¹). Experimentally, we clearly observe 3 medium strength bands in this region (see Fig. 3). Based on the DFT calculations they are readily assigned to umbrella CF₃ (experimentally observed at 729 cm⁻¹); CH out of plane deformation (experimentally observed at 791 cm⁻¹); ring deformation together with antisymmetric C–C stretch of terminal (C1–C2 and C4–C5 bonds) groups (experimentally observed at 861 cm⁻¹). Closer look at experimental spectrum in 1000–650 cm⁻¹ region (see Fig. 3,

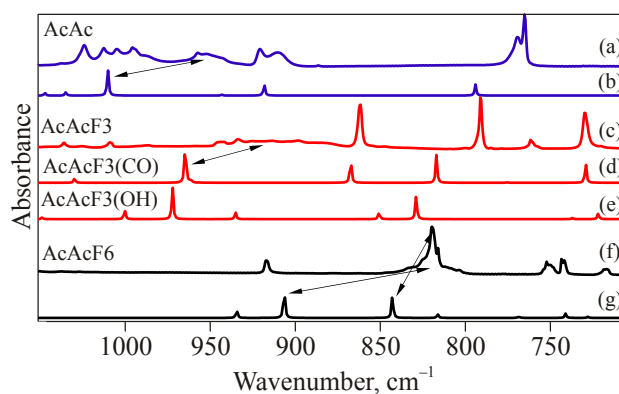


Fig. 3. Infrared absorption of argon matrix isolated and DFT calculated spectra of: AcAc (a) experimental, (b) calculated, AcAcF3 (c) experimental, AcAcF3(CO) (d) calculated, AcAcF3(OH) (e) calculated, AcAcF6 (f) experimental, (g) calculated.

spectrum (c)) allows us to identify one more, very broad band centered at 910 cm⁻¹ with complicated internal structure and width around 80 cm⁻¹. Based on B3LYP calculations this band is assigned to out of plane deformation (γ OH) band of AcAcF3(CO).

The assignment of the band is in agreement with previous observations of this band in argon [21], neon and parahydrogen [19]. In neon and parahydrogen matrices this band is observed as a narrow band with well defined position at 883.9 cm⁻¹ in Ne and at 882.5 cm⁻¹ in parahydrogen matrix while in argon it is a broad band centered at 910 cm⁻¹ with several ill defined peaks both in our experiments and in Ref. 21. One of the possible explanations is the higher temperature of the argon matrix experiments (above 10 K in our study and 15 K in Ref. 21) compared to those of neon (below 8 K) [19] and parahydrogen (below 4 K) [19]. Another probable reason for the band broadening is a more interacting argon environment perturbing out of plane vibration more extensively than neon and parahydrogen hosts.

The experimentally observed absorption spectra of AcAc and its fluorinated derivatives allow us to use experimental data to qualitatively evaluate how the hydrogen bond strength changes with the fluorination of the molecule. One of the most common ways to evaluate hydrogen bond strength is through the broadness and wavenumber red shift of the OH stretch band [18]. Unfortunately, we cannot directly apply this in the case of AcAc and its derivatives. As mentioned before the OH stretch band in AcAc and its fluorinated derivatives is so broadened that it is impossible to identify it precisely in the infrared absorption spectrum. Another two good candidates for the estimation of hydrogen bond strength could be in the in-plane OH deformation δ OH and out of plane deformation γ OH vibrational modes [18].

More detailed analysis of calculated modes of AcAc and its derivatives revealed that δ OH vibration is always

strongly coupled with other vibrations in the molecule, namely ring deformation, CH₃ deformation and CF₃ deformation vibrations, therefore it is impossible to find one band involving only δ OH in the AcAc and its fluorinated derivatives suitable for the comparison of these three molecules. On the contrary, the γ OH vibration in all three molecules is highly localized based on the DFT calculations and thus is suitable for the hydrogen bond strength comparison.

For the deformational vibrations, band wavenumber should decrease with the decrease of the hydrogen bond strength. The absorption band corresponding to γ OH vibration is easily identified in AcAc as doublet at 950 and 956 cm⁻¹ based on theoretical calculations and is in very good agreement with previous observations [7,11]. It is more difficult to assign this band for fluorinated AcAc molecules. For AcAcF₃ we observe a band centered at 910 cm⁻¹ with complicated internal structure and width around 80 cm⁻¹, the observation is in a good agreement with previous studies in argon [21], and gas phase [23]. For the AcAcF₆ it is even harder to identify experimental absorption band corresponding to γ OH. Curve fitting procedure performed in OPUS software allowed us to identify broad band centered at 821 cm⁻¹ with width of 20 cm⁻¹ and underneath the much narrower band at 819 cm⁻¹. The band position of γ OH vibration in the spectra shows increasing hydrogen bond strength in the order AcAcF₆, AcAcF₃ and AcAc, with AcAc being the strongest one.

Theoretical calculations predict two different isomers of AcAcF₃ depending on which side of the molecule CF₃ group resides (Table 1). The experimental spectra of pure AcAcF₃ isolated in argon and nitrogen matrices are compared to the calculated spectra of both possible isomers: AcAcF₃ with CF₃ group on CO side (AcAcF₃(CO)) and AcAcF₃ with CF₃ group on OH side (AcAcF₃(OH)) (see Fig. 4) in order to determine whether the two conformers

coexist in the matrix or if we only observe one of them. One of the most distinct difference in the calculated spectra between two isomers are wavenumbers and relative intensities of the corresponding C=O/C=C and C-C=C stretching vibrations in the 1700–1600 cm⁻¹ spectral region. In the experimental spectra of AcAcF₃ isolated in argon we observe one strong band at 1609 cm⁻¹ and broad weak band at 1647 cm⁻¹. The wavenumbers of these two bands and their relative intensities indicate that AcAcF₃(CO) is the only isomer present in the argon matrix. The correspondence between the calculated spectra of AcAcF₃(CO) isomer and experimental spectrum of AcAcF₃ in argon in the spectral range between 1550 and 1000 cm⁻¹ is not perfect, but overall comparison of band pattern in calculated and experimental spectra suggests the existence of only one isomer in argon matrix. Calculations in the spectral range between 1000 and 700 cm⁻¹ predict four medium strength bands for AcAcF₃(CO) isomer.

Experimentally we also observe four medium strength bands in this region. This also confirms the presence of a sole isomer. The assumption that only one isomer is present is consistent with previous findings [19,21]. The spectral pattern of AcAcF₃ changes when this molecule is isolated in nitrogen matrix compared to that of argon. Three significant spectral changes occur. In the C=O/C=C spectral region of AcAcF₃ isolated in nitrogen we observe the appearance of the spectral band at 1664 cm⁻¹. The inset of Fig. 4 allows to inspect this region in more detail. The band at 1607 cm⁻¹ in nitrogen and 1609 cm⁻¹ in argon is attributed to C-C=C stretch mode of the most stable isomer AcAcF₃(CO). This is in agreement with previous works [19,21]. This band is slightly red shifted in nitrogen in comparison to argon. The band at 1664 cm⁻¹ we observe in nitrogen is blue shifted from the bands observed in argon. This allows us to state that this band is a new band without corresponding absorption in argon.

The band position is in a good agreement with calculated C=O/C=C stretch band of AcAcF₃(OH) isomer. In order to support this we have compared the calculated and experimental difference between the two strongest bands of the possible isomers: C-C=C stretch band of AcAcF₃(CO) and C=O/C=C stretch band of AcAcF₃(OH). The wavenumber difference between C-C=C stretch band of AcAcF₃(CO) and C=O/C=C stretch band of AcAcF₃(OH) in calculated spectra is 60 cm⁻¹ and in the experimental spectra (nitrogen matrix) we observe 57 cm⁻¹ difference between C-C=C stretch at 1607 cm⁻¹ and the band at 1664 cm⁻¹. This allows to attribute this band to C=O/C=C stretch mode of AcAcF₃(OH). The intensity pattern is also consistent with the observation of AcAcF₃(OH) isomer as the 1664 cm⁻¹ band is one of the most intense bands of this isomer.

Another possible band of AcAcF₃(OH) in this spectral region is C-C=C stretch, but calculations predicts that it is two times weaker than the C=O/C=C band and the position is in between of the C=O/C=C stretch band of AcAcF₃(OH)

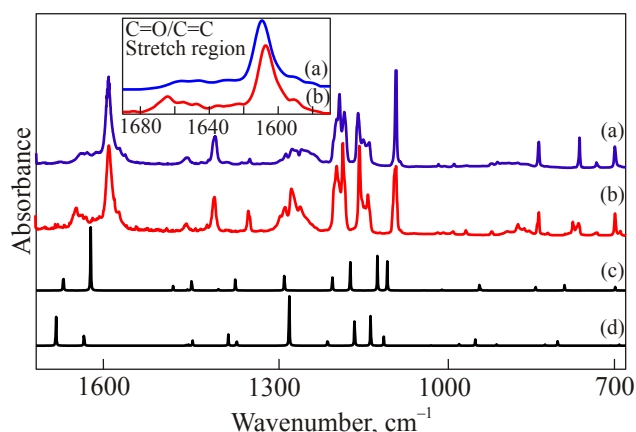


Fig. 4. Infrared absorption spectra of AcAcF₃ in (a) argon matrix, (b) nitrogen matrix and calculated spectra of (c) AcAcF₃(CO) and (d) AcAcF₃(OH). Experimental spectra are normalized to C-C=C stretch vibration (1609 cm⁻¹ argon/ 1607 cm⁻¹ nitrogen).

and C=C stretch of AcAcF3(CO). This region is perturbed by weak and broad band attributed to C=O/C=C stretch of AcAcF3(CO), which prevents clear identification of much weaker AcAcF3(OH) C=C stretch band.

Another strong feature observed in nitrogen matrix but not in argon, is the band at 1290 cm^{-1} . In argon we observe a broad band of medium strength in the same region. In nitrogen we observe additional strong band on top of the broad band. We believe that the observed band is a new feature as relative intensity grows significantly compared to the other bands. This observation is also consistent with the appearance of the second isomer in nitrogen matrix. The third spectral feature observed in nitrogen but not in argon matrix is the band at 802 cm^{-1} attributed to the mode from $\gamma\text{CH}/\rho\text{CH}_3$ vibrations of AcAcF3(OH). The same mode of AcAcF3(CO) isomer is observed in argon at 791 cm^{-1} and in nitrogen at 792 cm^{-1} . The calculations predict 12 cm^{-1} difference of $\gamma\text{CH}/\rho\text{CH}_3$ mode wavenumber in AcAcF3(CO) and AcAcF3(OH) isomers and experimentally we observe two bands in nitrogen with 10 cm^{-1} difference.

The fact that we do not observe less stable isomer of AcAcF3 in argon matrix can be explained by rapid tunneling of hydrogen atom between two sides of the molecule, which is occurring even in the low-temperature argon matrix. Thus at the lowest temperatures only the most stable isomer of AcAcF3 prevails. The fact that large amplitude motions are preserved in the inert gas matrices is in accordance with previous studies on acetylacetone molecules [16,19]. The more interacting nitrogen matrix inhibits hydrogen tunneling thus preserving both isomers in the low-temperature nitrogen matrix.

The calculated and experimental band intensities allow us to get approximate ratio of AcAcF3(CO) and AcAcF3(OH) isomers in nitrogen matrix. We performed two separate calculations: first one calculating band intensity ratio between $\nu\text{C}=\text{O}/\text{C}=\text{C}$ mode of AcAcF3(OH) and $\nu\text{C}-\text{C}=\text{C}$ mode of AcAcF3(CO) (bands at 1664 and 1607 cm^{-1} correspondingly); second one calculating band intensity ratio between $\gamma\text{CH}/\rho\text{CH}_3$ vibrational modes belonging to AcAcF3(OH) and AcAcF3(CO) isomers (bands at 802 and 792 cm^{-1} correspondingly). Both calculations resulted in the same estimation of isomers: 62% of AcAcF3(CO) and 48% of AcAcF3(OH). The DFT calculations estimated 5.4 kJ/mol energy difference between the two isomers, AcAcF3(CO) being the lower energy one. Based on this energy difference Boltzmann distribution at room temperature between two conformers is 89% of AcAcF3(CO) and 11% of AcAcF3(OH).

There might be a few explanations for this discrepancy: a) B3LYP calculations are overestimating the energy difference between isomers and b) the interaction with surrounding N_2 molecules stabilizes the less stable isomer. It is hard to discriminate which is the true reason for the higher abundance of the less stable isomer. The literature data indicates that depending on the method used estimated isomer

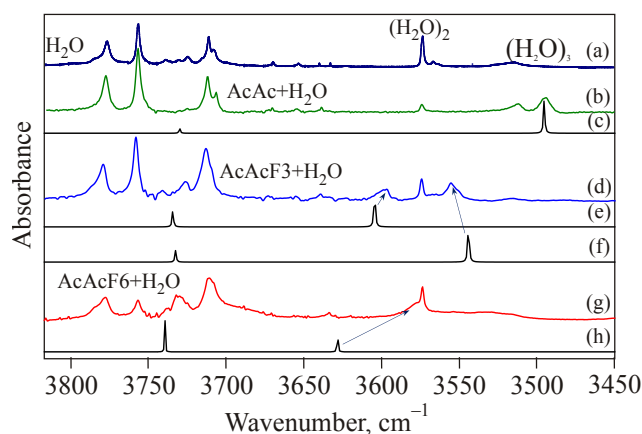


Fig. 5. IR absorption spectrum of (a) water in argon matrix (1:500), (b) acetylacetone and water in argon matrix (1:1:500), (c) calculated AcAc+H₂O spectrum, (d) IR absorption spectrum of trifluoroacetylacetone and water in argon matrix (1:1:500), (e) calculated AcAcF3(CO)+H₂O and (f) calculated AcAcF3(OH) spectra, (g) IR absorption spectrum of hexafluoroacetylacetone and water in argon matrix (2:1:500), (h) calculated AcAcF6+H₂O spectrum. Scaling factor of 0.96 was used for all calculated spectra: (c); (e); (f); (h). All unscaled calculated wavenumbers are blue shifted with respect to experimental spectrum.

energy difference can range from 0.7 to 5.9 kJ/mol [22]. If the former figure is right then the experimentally observed distribution of isomers would be close to the calculated from Boltzmann distribution. Another reason to the higher AcAc(OH) isomer content in the nitrogen matrix than predicted from calculations, the stabilization of this isomer because of van der Waals complexes between AcAcF3 and nitrogen also cannot be neglected. In order to completely answer this question much deeper theoretical studies including molecular dynamics are needed.

3.2.2. Acetylacetone derivatives water complexes

Theoretical calculations predict that the most stable complex formed from one acetylacetone molecule and one water molecule has the structure where hydrogen of water molecule is bonded to oxygen of C=O group in acetylacetone molecule (see Table 2). This type of bonding geometry remains similar for all the acetylacetone derivatives, the only change being H₂O rotation away from CF₃ groups in AcAcF3(CO) and AcAcF6 (the molecules where CF₃ group is present at the same side of the molecule as the C=O group) because of repulsion between oxygen of water molecule and fluorine of AcAc molecule. Infrared absorption spectra in OH stretching region of water and water mixtures with AcAc, AcAcF3 and AcAcF6 isolated in argon matrix are presented in Fig. 5. The calculated band wavenumbers are summarized in Table 4.

Table 4. Calculated wavenumbers of two lowest energy isomers of trifluoroacetylacetone: AcAcF3(CO) and AcAcF3(OH) and their complexes with H₂O

Mode	AcAcF3(CO)	AcAcF3(CO)+H ₂ O	Mode	AcAcF3(OH)	AcAcF3(OH)+H ₂ O
	$\tilde{\nu}$, cm ⁻¹	$\tilde{\nu}$, cm ⁻¹		$\tilde{\nu}$, cm ⁻¹	$\tilde{\nu}$, cm ⁻¹
$\nu_{\text{free}}\text{OH (H}_2\text{O)}$		3889.8	$\nu_{\text{free}}\text{OH (H}_2\text{O)}$		3888.0
$\nu_{\text{bound}}\text{OH (H}_2\text{O)}$		3754.5	$\nu_{\text{bound}}\text{OH (H}_2\text{O)}$		3691.6
νCH	3246.5	3247.4			
			νCH	3241.0	3242.5
			νCH_3	3149.0	3152.8
$\nu\text{OH}/\nu\text{CH}_3$	3147.3	3148.0			
νOH	3134.2	3198.4			
$\nu_a\text{CH}_3$	3094.3	3095.6			
			νOH		3112.8
			$\nu_a\text{CH}_3$	3088.6	3087.1
$\nu_s\text{CH}_3$	3041.5	3042.7			
			$(\nu\text{OH}/\nu_s\text{CH}_3)_s$	3036.5	3034.1
			$(\nu\text{OH}/\nu_s\text{CH}_3)_a$	3030.5	
			$\nu\text{C=O}/\nu\text{C=C}$	1700.2	1693.9
$\nu\text{C=O}/\nu\text{C=C}$	1687.5	1679.0			
			$\nu\text{C-C=C}/\delta\text{OH}$	1651.6	1655.4
$\delta\text{OH (H}_2\text{O + AcAcF}_3)$		1648.7			
$\nu\text{C-C=C}/\delta\text{OH}$	1640.2	1630.0	$\delta\text{OH(AcAc)}/\delta\text{OH(H}_2\text{O)}$		1631.3
$\delta\text{OH}/\text{um CH}_3$	1496.9	1498.8			
			tw CH_3	1474.4	1477.7
tw CH_3	1471.7	1471.2			
			$\delta\text{OH}/\delta\text{CH}/\text{um CH}_3$	1470.2	1470.8
$\delta\text{OH}/\text{um CH}_3$	1464.6	1462.2			
			$\delta\text{CH}/\text{um CH}_3$	1463.2	1466.6
um CH_3	1418.4	1420.2			
			$\delta\text{OH}/\text{um CH}_3$	1401.0	1406.2
$\delta\text{OH}/\text{um CH}_3$	1388.7	1390.7			
			$\delta\text{OH}/\delta\text{CH}/ \text{um CH}_3$	1386.5	1387.4
$\delta\text{OH}/\nu\text{C-CF}_3$	1303.7	1298.5			
			$\delta\text{OH}/\delta\text{CH}/\nu\text{CF}_3$	1295.3	1294.5
			$\delta\text{CH}/\rho\text{CH}_3$	1228.5	1237.3
$\delta\text{OH}/\delta\text{CH}$	1220.3	1219.3			
νCF_3	1189.2	1189.6			
			νCF_3	1181.7	1184.8
			νCF_3	1153.8	1155.9
$\delta\text{CH}/\nu\text{CF}_3$	1142.0	1147.4			
			δCH	1131.0	1133.4
δCH	1125.0	1130.4			
tw CH_3	1060.9	1060.7			
			tw CH_3	1048.7	1052.7
ρCH_3	1029.7	1031.4			
			ρCH_3	1000.3	1007.3

			γOH	972.1	941.3
γOH	964.6	943.6			
Γ ($\delta\text{C}=\text{C}-\text{OH}$)	961.4	962.2			
			$\Delta/(\delta\text{C}=\text{C}=\text{O})/\rho\text{CH}_3$	935.1	943.5
$\nu\text{C}-\text{CH}_3/\nu\text{C}-\text{CF}_3$	867.4	869.6			
			$\Delta/\nu\text{C}-\text{CH}_3/\nu\text{C}-\text{CF}_3$	850.7	851.8
			$\gamma\text{CH}/\rho\text{CH}_3$	828.9	833.9
$\gamma\text{CH}/\rho\text{CH}_3$	817.0	816.9			
γCH	775.3	773.2			
			$\Gamma/(\gamma\text{C}=\text{C}-\text{OH})$	737.1	736.7
um CF_3	729.2	730.2			
			$\Delta/\text{um } \text{CF}_3$	721.8	723.0
			$\Gamma/\text{tw } \text{CH}_3$	608.9	610.3
tw CH_3	600.1	601.4			

Notes: ν — stretching, δ — in-plane deformation, γ — out of plane deformation, ρ — rocking, tw — twisting, um — umbrella, Δ — whole molecule in-plane deformation, Γ — whole molecule out-of-plane deformation vibrations.

In the spectral region corresponding to OH stretch vibrations we do not expect to see any bands associated to the vibrations of AcAc molecules as the OH stretch of AcAc, AcAcF3 and AcAcF6 are highly red shifted and broadened, thus impossible to be clearly identified in the absorption spectrum [7,19–21]. Comparison of the spectra of water and water mixed with AcAc, AcAcF3 and AcAcF6 reveals that in the spectra of mixtures, additional bands, not observed in pure water spectra, appear. The most straightforward assignment is that of AcAc–water complex band. The strong band at 3495 cm^{-1} appears in the spectra of water mixed with AcAc. Based on theoretical calculations this band is attributed to the bound OH stretch (water OH group involved in hydrogen bonding) vibration of H_2O molecule bonded to AcAc. This assignment is in good agreement with previous observations [24,25]. Medium strength shoulder band at 3706 cm^{-1} is attributed to the free OH stretch (water OH group not involved in hydrogen bonding) vibration of H_2O molecule bonded to AcAc.

The assignment of the AcAcF6 and AcAcF3 bands is not as straightforward. In case of AcAcF6–water complex calculations predict that free OH stretch of water is an intense band with similar wavenumber as in the AcAc–water complex. This allows us to assign the strong spectral band at 3711 cm^{-1} to the free OH stretch of water bound to AcAcF6. Calculations predict that bound OH stretch of water bonded to AcAcF6 is much less red shifted than in the case of AcAc–water complex. Based on theoretical predictions we expect to observe a low intensity band in the region around 3600 cm^{-1} . Identification of this band was not easy, in thick and concentrated samples it is possible to observe broad shoulder band on water dimer bound OH stretch band at 3576 cm^{-1} .

The situation is more complicated in the case of water bound to AcAcF3 molecule. In the OH stretch region be-

sides water bands we observe three additional bands which appear in the spectra of AcAcF3–water mixtures: the bands at 3545 , 3590 and 3711 cm^{-1} . Based on calculations and comparison to previous AcAc–water and AcAcF6–water complexes the band at 3711 cm^{-1} can be attributed to the free OH stretch of water bound to AcAcF3. The similarity of this band position in different AcAcF3–water and fluorinated AcAcF3–water complexes indicates that water free OH stretch is insensitive to the molecular structure water is bound to. However remaining two bands at 3590 and 3545 cm^{-1} seems to point to existence of two distinct structures of AcAcF3–water complexes. The theoretical calculations predict that the strongest hydrogen bond is in the structure of AcAcF3(OH)–water complex. Calculated hydrogen bond energy is 20.1 kJ/mol (see Table 2).

The second strongest hydrogen bond is in the structure of AcAcF3(CO)–water complex and the calculated bond energy 15.3 kJ/mol . It is interesting to note that despite of significant difference of intermolecular hydrogen bond strength (5.2 kJ/mol) between AcAcF3(OH)–water complex and AcAcF3(CO)–water complex overall electronic energy is only by 0.7 kJ/mol lower for the AcAcF3(CO)–water complex. Thus observation of complexes of both isomers at similar concentrations can be expected. Comparison of calculated and experimental spectra (Fig. 5) suggest assignment of the band at 3545 cm^{-1} to the AcAcF3(OH)–water complex, and the band at 3590 cm^{-1} to the AcAcF3(CO)–water complex. This assignment correlates well with calculated hydrogen bond strength of the complexes. AcAcF3(OH)–water complex with stronger hydrogen bond exhibits a larger bound OH stretch red shift from the free OH stretch, and weaker complex of AcAcF3(CO)–water has a smaller bound OH stretch wavenumber red shift.

Calculated spectra of both isomers of AcAcF3 hydrogen bonded to water do not allow to expect many differences

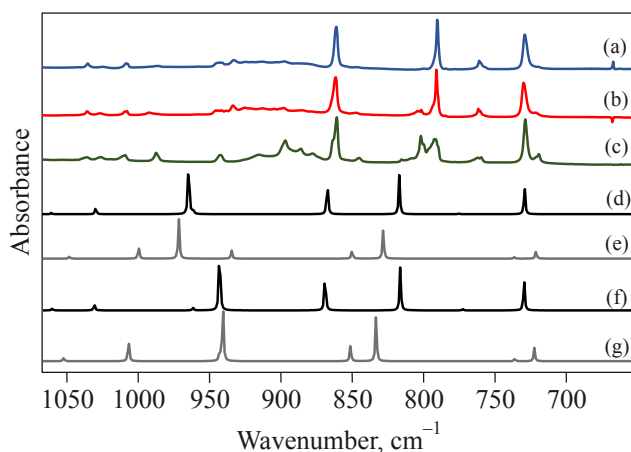


Fig. 6. IR absorption spectrum of (a) trifluoroacetylacetone in argon and (b) trifluoroacetylacetone and water in argon, (c) trifluoroacetylacetone in nitrogen, (d) calculated AcAcF3(CO), (e) AcAcF3(OH), (f) AcAcF3(CO) + H₂O and (g) AcAcF3(OH) + H₂O spectra.

between the spectra of pure AcAcF3 and AcAcF3 mixed with water (Table 4 and Fig. 6) in the “fingerprint” region of spectra. The most distinct bands in calculated spectra are bands around 900 cm⁻¹ attributed to the out of plane OH deformation band (γ OH) of AcAcF3 (compare Fig. 6 spectra (d) with (f) and (e) with (g)). Unfortunately, in the experimental spectrum of AcAcF3, the γ OH band is very ill defined. The band is broad and has structure of several underlying bands. The same band shape and structure is observed in both spectra of pure AcAcF3 and of AcAcF3 mixed with water in argon matrix (Fig. 6, spectra (a) and (b)). The band is likely to be broadened by strong coupling to the low wavenumber vibrations of CH₃ and CF₃ groups and is much more complicated than in the parent AcAc molecule.

The same broad and complicated γ OH band structure is also observed in the AcAcF6 molecule (Fig. 3). The one clearly notable difference between spectra of pure AcAcF3 and AcAcF3 mixed with water in argon matrix in the lower wavenumber range is the appearance of band at 801 cm⁻¹ in the spectra of AcAcF3 mixed with water. This band cannot be assigned to the pure AcAcF3(CO) or AcAcF3(CO)–water complex, but based on calculated spectra it can be associated with γ CH/ ρ CH₃ vibrational mode of the AcAcF3(OH) or AcAcF3(OH)–water complex. The appearance of the new band at 801 cm⁻¹ in argon matrix is consistent with the observations in OH stretch region where we have identified two bands corresponding to AcAcF3(CO)–water and AcAcF3(OH)–water complexes. The observation of the two bands in argon matrix of AcAcF3 mixtures with water at 801 and 791 cm⁻¹ is in agreement with the data of pure AcAcF3 isolated in nitrogen matrix where both isomers were confirmed to coexist. This observation allows to conclude that formation of hydrogen bond between water and AcAcF3(OH) isomer stabilizes

this isomer due to stronger intermolecular bond than in the case of AcAcF3(CO)–water complex and both isomers coexist in argon matrix when complex with water is formed.

In both structures water donates hydrogen to AcAcF3 C=O group. The most notable spectral effects are observed for water OH stretch vibrations. Their red shifts are comparable to the ones observed in formation of water dimers. However no significant spectral shifts are identified for the spectral bands of AcAcF3. This is in slight contradiction to AcAc where *ca* 20 cm⁻¹ red shift is observed for γ OH vibrations. However even in the case AcAc the shifted band associated to the formation of AcAc–water complex is broad and weak. In the case of AcAcF3 the γ OH band is much broader and weaker than in AcAc (see Fig. 3), AcAc band width is 20 cm⁻¹ and AcAcF3 the bandwidth is around 80 cm⁻¹ with complicated internal structure. These circumstances explain why it is not possible to observe weaker and less red shifted γ OH band of AcAcF3–water complex.

The studies of AcAcF3 mixture with water isolated in nitrogen revealed similar picture as in the case of argon. The spectra in the OH stretch region of nitrogen isolated AcAcF3 mixture with water are presented in Fig. 7 spectrum (b). The pure water spectrum in nitrogen is added for comparison (spectrum (a) in Fig. 7). As in the case of argon in nitrogen we also do not expect to see any bands from pure AcAcF3 in this region. In the spectra of AcAcF3 and water mixture we observe three additional bands that did not appear in the spectrum of pure water. The same situation was observed in argon matrix as well. Based on calculations the strongly growing band at 3701 cm⁻¹ is assigned to the free OH stretch band of water bound to AcAcF3 molecule. In both possible isomers AcAcF3(OH)–water and

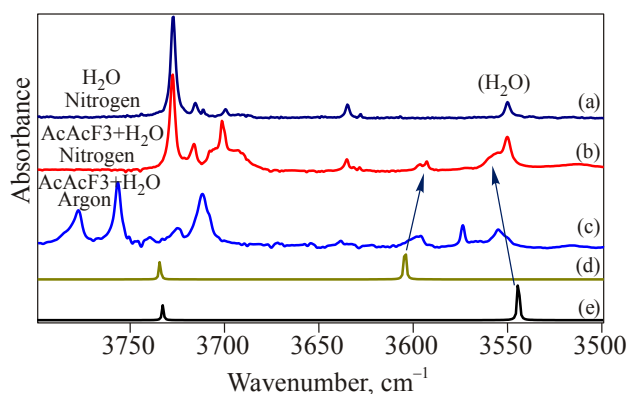


Fig. 7. IR absorption spectrum in the OH stretch region of (a) water in nitrogen matrix (1:500), (b) trifluoroacetylacetone and water in nitrogen matrix (1:1:500), (c) trifluoroacetylacetone and water in argon matrix (1:1:500), (d) calculated AcAcF3(CO) + H₂O and (e) calculated AcAcF3(OH) spectra. Scaling factor of 0.96 was used for all calculated spectra: (d); (e). All unscaled calculated wavenumbers are blue shifted with respect to experimental spectrum.

AcAcF₃(CO)–water, the calculated position is very similar, 3889.8 cm⁻¹ for AcAcF₃(CO)–water and 3888.0 cm⁻¹ for AcAcF₃(OH)–water isomer, therefore it is highly possible that both isomers are contributing to the experimental band.

The other two observed bands are: the doublet with peaks at 3595 and 3593 cm⁻¹ and broad band at 3555 cm⁻¹ perturbed by the water dimer band at 3550 cm⁻¹. The spectral pattern and absolute band positions of water bound OH stretch of AcAcF₃–water complex in nitrogen are very similar to those observed in argon. Based on calculations and argon data, band at 3555 cm⁻¹ is assigned to AcAcF₃(OH)–water complex and doublet at 3595 and 3593 cm⁻¹ to AcAcF₃(CO)–water complex. The band width and relative intensity of the doublet is slightly changing during annealing process, but the intensity ratio remains constant in different concentration of water to AcAcF₃ experiments, suggesting that the observed doublet is an effect of different trapping sites in matrix for the same AcAcF₃–water isomer. These observations allow to conclude that in nitrogen we observe the same two isomers of AcAcF₃–water complex as in argon.

Conclusions

Infrared absorption spectra of trifluoroacetylacetone and trifluoroacetylacetone–water mixtures isolated in nitrogen and argon matrices were studied. The results from these studies were compared with the studies of similar molecular compounds acetylacetone and hexafluoroacetylacetone. The experimental and calculated data revealed that only one of the two possible chelated enol isomers of trifluoroacetylacetone — the one with CF₃ group on C=O side of the molecule exists in argon matrix. The studies in nitrogen matrix revealed that both isomers with CF₃ group on C=O side and CF₃ group on OH side coexist in this matrix in approximately equal concentrations. The addition of water leads to the trifluoroacetylacetone–water complex formation. This is well manifested in the appearance of new bands in the OH stretch region attributed to the free and bound OH stretches of the water molecule bonded to trifluoroacetylacetone.

The analysis of the calculated and experimental spectra leads to the conclusion that complexes of water with both isomers of trifluoroacetylacetone coexist in argon and nitrogen matrices. It allowed us to conclude that association with water stabilizes the less stable isomer with CF₃ group on OH group side of trifluoroacetylacetone molecule.

The comparison of water, bonded to acetylacetone, hexafluoroacetylacetone and trifluoroacetylacetone, bound OH stretch vibration wavenumber red shift allowed to conclude that water forms strongest hydrogen bond with acetylacetone, a weaker one with trifluoroacetylacetone and the weakest one with hexafluoroacetylacetone. These experimental observations are in good agreement with calculated complex binding energies. The formation of hydro-

gen bond with water slightly weakens the internal hydrogen bond of the trifluoroacetylacetone based on theoretical calculations; however the experimental data does not allow us to detect the perturbation of trifluoroacetylacetone vibrations from formation of hydrogen bond with water due to the highly broadened bands involving OH vibrations.

Acknowledgments

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Вплив навколишнього середовища та асоціації
з водою на внутрішню структуру
трифторацетилацетона.
FTIR дослідження матричної ізоляції

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Структуру трифторацетилацетона в матрицях аргону й азоту та його взаємодію з молекулами води вивчено за допомогою FTIR спектроскопії та розрахунків теорії функціонала густини (DFT). Смуги поглинання трифторацетилацетона, ізолюваного в аргоні, можна віднести до одного конформера 1,1,1-трифтор-4-гідрокси-3-пентен-2-ону (AcAcF₃(CO)), що добре узгоджується з попередніми дослідженнями. Смуги поглинання трифторацетилацетона, ізолюваного в азотній матриці, неможна пояснити присутністю тільки одного конформера, та за допомогою DFT розрахунків було підтверджено, що обидва конформера 1,1,1-трифтор-4-гідрокси-3-пентен-2-он та 5,5,5-трифтор-4-гідрокси-3-пентен-2-он (AcAcF₃(OH)) співіснують в азотній матриці. Додавання води до суміші трифторацетилацетон–матриця призводить до появи нових спектральних смуг, які не належать ні трифторацетилацетону, ні водним мономерам, що підтверджує утворення комплексів

трифторацетилацетон–вода. Було виявлено, що найбільш поширеним ізомером з комплексів трифторацетилацетон–вода є той, який утворюється з 5,5,5-трифтор-4-гідрокси-3-пентен-2-она і води, приєднаної до його групи C=O в обох матрицях. Комплекс 1,1,1-трифтор-4-гідрокси-3-пентен-2-он–вода спостерігається в менших кількостях.

Ключові слова: матрична ізоляція, водні комплекси, ацетилацетон, трифторацетилацетон.

Влияние окружающей среды и ассоциации
с водой на внутреннюю структуру
трифторацетилацетона.
FTIR исследования матричной изоляции

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Структура трифторацетилацетона в матрицах аргона и азота и его взаимодействие с молекулами воды изучены с помощью FTIR спектроскопии и расчетов теории функционала плотности (DFT). Полосы поглощения трифторацетилацетона, изолированного в аргоне, можно отнести к одному конформеру 1,1,1-трифтор-4-гидрокси-3-пентен-2-ону (AcAcF₃(CO)), что хорошо согласуется с предыдущими исследованиями. Полосы поглощения трифторацетилацетона, изолированного в азотной матрице, не могут быть объяснены присутствием только одного конформера, и с помощью DFT расчетов было подтверждено, что оба конформера 1,1,1-трифтор-4-гидрокси-3-пентен-2-он и 5,5,5-трифтор-4-гидрокси-3-пентен-2-он (AcAcF₃(OH)) сосуществуют в азотной матрице. Добавление воды к смеси трифторацетилацетон–матрица приводит к появлению новых спектральных полос, не принадлежащих ни трифторацетилацетону, ни водным мономерам, что подтверждает образование комплексов трифторацетилацетон–вода. Было обнаружено, что наиболее распространенным изомером из комплексов трифторацетилацетон–вода является тот, который образуется из 5,5,5-трифтор-4-гидрокси-3-пентен-2-она и воды, присоединенной к его группе C=O в обеих матрицах. Комплекс 1,1,1-трифтор-4-гидрокси-3-пентен-2-он–вода наблюдается в меньших количествах.

Ключевые слова: матричная изоляция, водные комплексы, ацетилацетон, трифторацетилацетон.