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Conformation and vibrational spectra and assignment of 2-thenoyltrifluoroacetone

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ABSTRACT

The conformational stabilities of different tautomers of 2-thenoyltrifluoroacetone (4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione, TTFA) in several solutions have been investigated at the B3LYP level using 6-311++G^{**} basis set. The self-consistent Onsager reaction field model was used to study the solvent effects. It was determined that the energy differences of the most stable conformers (stabilized by the hydrogen bridge), which are negligible in the gas phase, increase in the solvent media. The harmonic vibrational frequencies were calculated at the B3LYP level using 6-31G^{**} and 6-311G^{**} basis sets. A complete vibrational assignment has been clearly provided for the experimental IR and Raman spectra of TTFA and its deuterated analogue, which shows coexisting of four conformations in the sample. This vibrational spectroscopy analyses confirms more content of the "A" forms in the solution than the "B" forms, although the reverse is true in the solid state, in agreement with the theoretical DFT calculations and the experimental X-ray results.

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1. Introduction

By understanding the keto-enol tautomerism, it is straightforward to show that a β -diketone can transform bidirectionally into two cis-enol forms as illustrated in Fig. 1. In these cis-enol forms, because of the spatial shape of the molecule, it is possible for the hydrogen atom of the hydroxyl group to lie in a suitable orientation and distance for encountering an intramolecular hydrogen bond (IHB). The strong IHB stabilizes the cis-enol form of the β diketone [1–4]. The hydroxyl, carbonyl, and alkene functional groups involved in the enol forms contain six atoms that can contribute in a π -electronic resonance conjugation to induce a ring like structure, which is referred to as a chelated ring. The remarkable aim here is to crosscheck the effects of different α or β -substitutions on the stability and IHB strength of each of the mentioned conformers. Malonaldehyde, MA, and acetylacetone, AA, are the simplest β -dicarbonyls (β -dialdehyde and β -diketone, respectively) and several experimental and theoretical studies have proven their asymmetrical structures due to the strong IHB in their most stable conformers, the chelated cis-enol forms [4–11].

Vibrational spectra of numerous molecules of this category have been extensively investigated, where the existence of a strong

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intramolecular hydrogen bond has been established in the chelated cis-enol tautomers [9–29].

Any factor which affects the electronic properties of the chelated ring will change the intramolecular hydrogen bond strength and the tautomerization equilibrium. Whenever R_1 and R_3 substitutions are electronically different, one of the two cis-enol forms is more stable. This fact has been established by theoretical and experimental studies such as quantum-mechanical calculations, IR, Raman, microwave, and NMR spectroscopies, X-ray, electron, and neutron diffraction measurements of AA and its derivatives [10–16,30–37].

Additional studies have shown that the IHB strength increases when a bulky group is posited in α position [38–42]. Several experimental studies suggest that the substitution of electron-withdrawing groups, such as trifluoromethyl ($-CF_3$), in β position, weakens the IHB, while the electron supplying groups such as phenyl ($-C_6H_5$) make IHB stronger [16,34,43–45].

Many β -dicarbonyl compounds exist exclusively in an enol structure in the solid state [18,46–49]. C₄H₃S–COCH₂CO–CF₃, 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione, known as 2-thenoyltrifluoroacetone (TTFA), is also in the enol form in the solid state as indicated by X-ray diffraction data. The unit cell consists of two molecules, which have slightly different geometrical structures [50]. According to the X-ray results, the enolization is favored near to the electron-withdrawing –CF₃ group, i.e. B2 conformer. TTFA has two β -substituted groups with different

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Fig. 1. The keto-enol tautomerism leads to two different chelated enol forms for asymmetric β -dicarbonyls.

electron-withdrawing, steric, and resonance effects; hence in our previous work [24] the effects of these substitutions on stability and intramolecular hydrogen bond strength and also on the structure of molecule have been investigated. There, it was shown that among 40 possible conformers of TTFA only four cis-enol chelated conformers are engaged in the IHB system. Between these conformers (A1, A2, B1, and B2), MP2 calculations showed that the B2 conformer in which the hydroxyl group is in the –CF₃ side is significantly more stable than others (see Fig. 2), which is in line with the X-ray diffraction results.

The present paper is a continuance of our aforementioned work. Since the vibrational spectroscopy is a highly sensitive technique to experimentally examine the hydrogen bonding and interaction with solvents, therefore we used this data as the empirical witness. Since the stable conformers in solution may differ from gaseous and solid states, the theoretical prediction could be very helpful for a clear spectral assignment. This paper predicts the conformational stabilities in solution and the vibrational characteristics (such as harmonic fundamental band wavenumbers and corresponding intensities of IR and Raman spectra) of TTFA by means of density functional theory (DFT) level. The calculated harmonic force constants of TTFA were used for predicting the Raman and IR spectra of deuterated analogue, D2-TTFA. The calculated vibrational frequencies for the predicted most stable conformers in different media are compared with those observed experimentally. To our knowledge, no vibrational spectroscopic data has been reported for TTFA. In this report, we present a clear vibrational assignment of TTFA by considering the IR and Raman spectra of its deuterated analogue and theoretical calculations.

2. Experimental

TTFA was purchased from Aldrich chemical company with the purity of 99% in the solid form and was purified by sublimation.



Fig. 2. Possible chelated cis-enol tautomers of TTFA and their relative stability at $\text{MP2}/\text{6-31G}^{**}.$

 D_2 -TTFA was prepared by dissolving the non-deuterated molecule in a mixture of dry CCl₄ and D_2O (5:1). After a few hours, the aqueous phase was removed in a nitrogen filled glove box and this approach was repeated three times. The final organic phase was dried over P_2O_5 and then the solvent was removed under vacuum in order to crystallize D_2 -TTFA.

The mid-Infrared spectra were obtained in the range of 4000– 500 cm^{-1} with spectral resolution of 2 cm⁻¹ by averaging the results of 20 scans on a Bomem MB-154 Fourier Transform Spectrophotometer.

The far-Infrared spectra in the $500-50 \text{ cm}^{-1}$ region were collected employing a Thermo Nicolet NEXUS 870 FT-IR spectrometer equipped with a DTGS/polyethylene detector and a solid substrate beam splitter. The spectra were collected with a resolution of 4 cm⁻¹ by averaging the results of about 60 scans.

All FT-Raman spectra from 3500 to 170 cm^{-1} were recorded using a 180° back-scattering geometry and a Bomem MB-154 Fourier Transform Raman spectrometer. It was equipped with a ZnSe beam splitter and a TE cooled InGaAs detector. Rayleigh filtering was afforded by a set of two holographic technology filters. Laser power at the samples was 300 MW. The spectra were collected with a resolution of 4 cm⁻¹ by coadding the results of about 1000 scans.

All spectra were measured at room temperature. The solid samples for IR were examined as KBr discs and solution spectra were considered in CCl_4 , CS_2 , and CH_3CN solutions.

3. Method of analysis

All quantum calculations were carried out with the GAUSSIAN 03 software package [51], applying the modern density functional theory, DFT method. The hybrid gradient-corrected (three-parameter nonlocal) exchange functional by Becke [52] with the gradient corrected (nonlocal) correlation functional of Lee et al. [53] was selected.

In our previous study on TTFA [24], all the possible enol and keto conformations of molecule have been fully optimized and the results were discussed. In this work, the self-consistent Onsager reaction field model [54-55] was used to study the solvent effects on the four most stable chelated cis-enol tautomers of TTFA. In this approach, a solute molecule with a certain dipole moment is placed in a spherical cavity in a polarizable continuum, representing the solvent, with a dielectric constant (ε). The cavity sizes were calculated from molecular volumes. Specific solute-solvent effects are not taken into account at this level of calculation and the obtained solvation energies correspond to the electrostatic contributions, which, however, play a dominant role in tautomerization reactions [56]. These solvent calculations were performed at the B3LYP level of DFT theory using the 6-311++G** basis set, which is a triple-zeta split valence set augmented with polarization and diffused functions [57] on all atoms (351 basis functions, and 563 primitive Gaussians).

The calculations of vibrational frequencies and IR intensities for the A1, A2, B1 and B2 conformers and their deuterated species were achieved at the B3LYP/6-311G** level. The Raman intensities were calculated at the B3LYP/6-31G** level. The assignment of the calculated wavenumbers is aided by the animation option of GaussView 3.0 graphical interface [58] for Gaussian programs, which gives a visual presentation of the shape of the vibrational modes.

Vibrational normal modes of thiophene were also calculated at the B3LYP/6-311G** level of theory. The notations for 2-thienyl group vibrations are according to these theoretical normal modes of thiophene, which are illustrated by Molekel 4.3 program [59,60].

Lorentzian functions have been utilized for deconvolution of all IR and Raman spectra using Genplot package [61].

4. Results and discussions

4.1. Solvent influences

Theoretical calculation at the B3LYP level using a variety of basis sets have shown [24] that all chelated A and B conformers of TTFA have nearly the same stabilities in the gaseous phase (so that the highest energy difference between them except for B1, even at the B3LYP/6-311G** with the most different results, is less than 0.44 kcal/mol). However, these results are not reliable in solution states with the solvent of different polarities because the four chelated conformations have relatively different dipole moments and a solvent can enhance the energy differences between them.

In order to study the solvent influences on stability and structure of the molecule, several calculations on the chelated forms have been done in various solvents. As previously mentioned, to achieve this aim, the Onsager method [54–55] was applied with 6-311++G** basis set at the B3LYP level of theory. Initially, the recommended cavity radius for the SCRF calculation of each possible chelated conformation (a_0 = 4.62, 4.38, 4.60, and 4.54 Å for A1, A2, B1, and B2, respectively) was obtained from single point VOL-UME calculations. Then fully optimizations were performed for the SCRF calculations in carbon tetrachloride (CCl₄), 1,2-dichloroethane (Cl_2Eth), acetonitrile (CH_3CN), and dimethylsulfoxide (DMSO) as the solvents with different polarities, characterized by their dielectric permittivity constant (ε = 2.228, 10.36, 36.64, and 46.7, respectively). The results of relative stability energies for chelated cis-enol forms in solution, in comparison with the most unstable form in the gaseous state, B1, along with their calculated dipole moments in the gas and solution phases are summarized in Table 1. Predictably, the greater the dipole moment a conformation has, the greater the stability it can obtain in a more polar solvent. Fig. 3 shows that the energy differences of the chelated forms, which are negligible in their gaseous states, become quite noticeable as the medium polarity increases. This causes the contents of the B conformers to be underestimated compare to the A conformers in the solution. For instant, the relative energies of A1, B2, and B1 chelated forms with respect to A2 in CH₃CN and DMSO are about 1.3, 2.5, and 3.3 kcal/mol, respectively.

4.2. Vibrational analysis

The assignments of the experimental frequencies are based on the observed band frequencies and intensity changes in the Raman



Fig. 3. The solvent influence on the relative stability of TTFA chelated forms, in comparison with the gaseous state of B1 conformer, as a function of ε , predicted at B3LYP/6-311++G^{**}.

and infrared spectra of the deuterated species, confirmed by establishing one to one correlation between the observed and the theoretically calculated frequencies. The calculated harmonic vibrational band frequencies and their approximate assignments for the enol forms of TTFA and their corresponding deuterated analogous, D₂-TTFA, along with the observed infrared and Raman frequencies are listed in Tables 2 and 3, respectively. The IR spectra of TTFA and D₂-TTFA in the OH/OD stretching region are compared in Fig. 4. The IR and Raman spectra of TTFA and D₂-TTFA in the region below 1700 cm⁻¹ are compared in Figs. 5 and 6, respectively. The IR spectra of TTFA in the solid state and in the CCl₄ solution are compared in Fig. 7. The deconvoluted IR spectrum of TTFA in the 1350–830 cm^{-1} region is presented in Fig. 8. Lorentzian functions have been utilized for deconvolution of the IR and Raman spectra. The notations for thienyl group vibrations are according to the characterization of vibrational normal modes of thiophene, which are illustrated in Fig. 9. The calculated frequencies are slightly higher than the observed values for the majority of the normal modes. In addition to the error of the theoretical method used, the difference between the computed and experiment frequencies may be due to many different factors that are usually not even considered in the theory, such as anharmonicity, Fermi resonance, solvent effects, etc.

4.2.1. CH stretching modes

The only CH bonds in the molecule are those of thienyl ring and that of the α -position in the chelated (enol) ring. In contrast with the latter, the formers are not affected by deuteration of the molecule. The deconvoluted Raman spectrum of TTFA indicates six bands at 3117, 3112, 3108, 3101, 3095, and 3084 cm⁻¹. It will be shown that the existence of these bands could be well attributed to the presence of the four most stable tautomers of TTFA (A1, A2, B1, and B2) in comparable amounts in the sample. As shown in Tables 2 and 3, this is well supported with the presence of other

Table 1

The relative stability energies for chelated cis-enol conformers of TTFA in comparison with the gaseous B1 (in kcal/mol), and their dipole moment (Debye) in several solvent at B3LYP/6-311++G** level of theory.

| | Relative ene | rgy | | | Dipole mo | Dipole moment | | | | | | | |
|----|--------------|------------------|---------------------|--------------------|-----------|---------------|------------------|---------------------|--------|--------|--|--|--|
| | Gas | CCl ₄ | Cl ₂ Eth | CH ₃ CN | DMSO | Gas | CCl ₄ | Cl ₂ Eth | CH₃CN | DMSO | | | |
| A1 | -0.706 | -2.165 | -4.150 | -4.775 | -4.834 | 6.043 | 7.290 | 9.078 | 9.661 | 9.702 | | | |
| A2 | -0.767 | -2.513 | -5.142 | -6.040 | -6.127 | 6.024 | 7.527 | 10.009 | 10.815 | 10.876 | | | |
| B1 | 0.000 | -0.991 | -2.312 | -2.717 | -2.755 | 4.983 | 5.951 | 7.270 | 7.685 | 7.722 | | | |
| B2 | -0.653 | -1.707 | -3.151 | -3.559 | -3.600 | 5.050 | 6.040 | 7.437 | 7.852 | 7.883 | | | |

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 Table 2

 Fundamental band assignment of TTFA (frequencies in cm⁻¹).^a

| Theoretical | | | | | | | | | | | | Experimen | tal | | Assignment | |
|--------------|-----------------|----------------|--------|--------------|----------------|------|--------------|----------------|------|--------------|----------------|----------------------|-----------------------|----------------------|----------------------|---|
| A1 | | | A2 | | | B1 | | | B2 | | | IR | | Raman | | |
| Freq | I _{IR} | A _R | Freq | $I_{\rm IR}$ | A _R | Freq | $I_{\rm IR}$ | A _R | Freq | $I_{\rm IR}$ | A _R | CCl ₄ | Solid | CCl ₄ | Solid | |
| | | | 3255 | 2 | 36 | | | | 3253 | 1 | 39 | 3121(3) | 3118(12) | 3117(6) | 3117(10) | νCH _α |
| 3246 | 1 | 204 | 3244 | 1 | 214 | 3244 | 0 | 207 | 3242 | 1 | 209 | 3114(4) | 3112(6) | 3112(5) | 3114(5) | 1 |
| 3241 2221 | 5 | 33 | | | | 3237 | 1 | 34 | | | | 3109(3) 2102(1) | 3109(10) 2102(5) | 3108(10) 2101(2) | 3110(12) 2100(5) | νCH _α |
| 5251 | 1 | 51 | 3220 | 1 | 102 | 5220 | 1 | 00 | 3219 | 2 | 102 | 3096(3) | 3094(9) | 3095(4) | 3094(7) | 2 |
| 3211 | 4 | 145 | 3207 | 4 | 82 | 3209 | 3 | 136 | 3206 | 5 | 87 | 3084(3) | 3085(7) | 3084(3) | 3085(5) | 13 |
| 3070 | 306 | 7 | 3028 | 327 | 6 | 3062 | 336 | 100 | 3080 | 340 | 115 | 2850(2) | n.c. | - | - | vOH |
| 1660 | 120 | 20 | | | | 1688 | 503 | 57 | 1685 | 537 | 59 | 1651(25) | 1657(47) | 1657(4) | 1656(8) | $v_a O = C - C = C + \delta O H$ |
| 1009 | 120 | 29 | 1662 | 170 | 135 | | | | | | | 1630(18) 1623(11) | 1639(40) 1624(35) | 1625(11) | 1638(7) 1621(9) | $v_a C = C = C = O + \delta O H$ $v_b C = C - C = O + \delta O H$ |
| 1641 | 802 | 360 | 1637 | 734 | 211 | | | | | | | 1601(36) | 1600(35) | 1594(25) | 1595(14) | $v_sC = C - C = O + \delta OH + vC - thio$ |
| | | | | | | 1631 | 46 | 181 | | | | 1583(29) | 1583(45) | 1584(20) | 1578(26) | $v_{s}O = C - C = C + \delta OH + vC - CF_{3}$ |
| | | | 1507 | 20 | 120 | | | | 1631 | 58 | 247 | 1583(29) | 1583(45) | 1584(20) | 1578(26) | $v_s O = C - C = C + \delta O H + 14 + v C - C F_3$ |
| | | | 1507 | 28 | 120 | 1562 | 96 | 45 | | | | 1522(7) 1519(4) | 1523(25) | 1524(13) 1520(15) | 1525(9) 1519(11) | $14 + \delta OH + \delta OH$ $14 + \delta OH + \delta CH_{a}$ |
| | | | | | | 1502 | 50 | 15 | 1563 | 36 | 10 | 1519(4) | 1520(29) | 1520(15) | 1519(11) | $14 + v_s(C=0,C-0) + vC-C + \delta CH_{\alpha}$ |
| 1552 | 30 | 59 | | | | | | | | | | 1508(1) | 1505(12) | 1504(5) | 1510(5) | $14 + v_a C = C - C + \delta OH + \delta CH_{\alpha}$ |
| 1489 | 134 | 2 | 1 40 4 | 204 | C | | | | | | | 1456(3) | 1457(10) | 1455(4) | 1456(5) | $vaO-C=C-C + \delta OH + \delta CH_{\alpha} + vC-CF_3 + 3$ |
| | | | 1484 | 204 | 6 | 1479 | 18 | 27 | 1476 | 43 | 37 | 1448(6) 1437(3) | 1447(22) 1436(8) | 1445(8) 1437(14) | 1448(9) 1440(13) | $v_{a}O - C = C - C + \delta OH + \delta CH_{\alpha} + v_{c} - CF_{3}$ |
| 1459 | 146 | 648 | 1456 | 80 | 732 | 1475 | 10 | 21 | 1470 | 45 | | 1437(3) 1414(21) | 1418(35) | 1412(100) | 1410(13) | 3 + vC = 0 |
| | | | | | | 1448 | 155 | 327 | 1448 | 147 | 282 | 1412(28) | 1407(55) | 1410(85) | 1406(100) | $3 + v_a(C=0,C-0) + \delta CH_{\alpha}$ |
| | | | 1419 | 30 | 12 | | | | | | | 1389(3) | 1388(7) | 1392(8) | 1387(9) | $v_{s}O-C=C-C+4+vC=O+\delta OH$ |
| 1400 | 70 | 15 | | | | 1408 | 127 | 61 | | | | 1370(4) | 1372(10) | 1370(8) | 1374(8) | $v_sC-C=C-O+\delta OH+vC=O$ |
| 1402 | /3 | 15 | | | | | | | 1401 | 70 | 298 | 1361(6) | 1365(15) 1369(10) | 1362(13) 1362(13) | 1361(15) | $v_{s}C - C = C - C + 4 + vC = 0 + \delta OH$ $v_{s}C - C = C - 0 + \delta OH + vC = 0$ |
| | | | | | | | | | 1385 | 37 | 11 | 1356(13) | 1361(36) | 1357(17) | 1358(24) | 4 |
| 1381 | 105 | 174 | | | | 1378 | 147 | 286 | | | | 1353(16) | 1358(43) | 1353(20) | 1354(34) | 4 + δOH |
| 1015 | 264 | 104 | 1363 | 81 | 43 | | | | | | | 1317(26) | 1315(63) | 1317(11) | 1318(15) | $4 + va(C-O,C=O) + \delta OH$ |
| 1315 | 364 | 164 | 1316 | 401 | 234 | | | | 1313 | 840 | 75 | 1283(30) 1279(41) | 1289(50) 1256(51) | 1287(19) | 1285(40) 1259(21) | $\delta OH + vC - CF_3 + vC = C + vC - thio + 15$ $\delta OH + vC = C + vC - CF_2 + vC - thio + 15$ |
| | | | | | | 1305 | 770 | 22 | 1313 | 040 | 75 | 1273(41) 1274(49) | 1254(56) | 1270(23) | 1253(21) 1254(22) | $\delta OH + vC = C + vC $ |
| 1265 | 85 | 14 | 1270 | 60 | 7 | 1266 | 42 | 5 | 1268 | 48 | 4 | 1252(28) | 1261(61) | 1251(18) | 1261(23) | $15 + \delta CH_{\alpha} + \nu C$ -thio + νC -CF ₃ |
| | | | | | | | | | 1249 | 75 | 15 | 1244(11) | 1240(30) | 1243(19) | 1239(14) | $15 + vC - CF_3 + \delta CH_{\alpha} + vC_4 - S$ |
| 1224 | 10 | n | 1238 | 185 | 15 | | | | | | | 1231(21) | 1233(35) | 1229(10) | 1234(13) | $15 + vC - CF_3 + \delta CH_{\alpha} + \delta OH + vC_4 - S$ |
| 1254 | 12 | Z | | | | 1215 | 10 | 3 | | | | 1231(21) 1222(8) | 1235(35) | - | 1234(13) | $15 + vC_4 - S + \delta CH_{\alpha} + vC_4 - S$ $15 + vC_4 - S + \delta CH_{\alpha} + vC_4 - S$ |
| | | | | | | 1194 | 354 | 3 | 1192 | 339 | 3 | 1205(71) | 1200(94) | - | 1195(10) | vaCF ₃ |
| 1189 | 276 | 1 | 1188 | 263 | 2 | | | | | | | 1199(69) | 1188(85) | - | 1191(15) | vaCF ₃ |
| 1170 | 284 | 3 | 1169 | 280 | 3 | 1171 | 200 | | 1171 | 200 | | 1165(100) | 1155(80) | - | 1163(10) | vaCF ₃ |
| | | | | | | 1171 | 296 88 | 4 | 1171 | 296 87 | 4 | 1162(44) 1110(71) | 1144(100) 1110(75) | - 1112(5) | 1163(10) 1113(8) | v_{ACF_3} $\delta CH_{11} + v_{1}CF_2 + vC_{-}O + 6$ |
| 1131 | 238 | 8 | 1131 | 222 | 12 | | 00 | - | 1152 | 0, | - | 1110(71) | 1110(75) | 1112(5) | 1113(8) | $\delta CH_{\alpha} + v_s CF_3 + v C - C + 6$ |
| 1110 | 16 | 25 | 1110 | 1 | 42 | | | | | | | 1084(9) | 1095(42) | 1082(39) | 1093(32) | 5 |
| | | | 1007 | | 4.0 | 1108 | 6 | 12 | 1109 | 7 | 18 | 1084(9) | 1084(31) | 1082(39) | 1082(25) | 5 |
| 1083 | 14 | 17 | 1087 | 23 | 16 | | | | 1085 | 30 | 6 | 1065(14) | 10654(58) | 1070(4) 1063(13) | 1072(8) 1064(15) | 6 |
| 1005 | 14 | 17 | | | | 1075 | 59 | 2 | 1005 | 55 | 0 | 1059(3) | 1051(35) | 1058(7) | 1054(4) | 6 + <i>v</i> C–C |
| 1049 | 80 | 1 | | | | | | | | | | 1032(12) | 1028(19) | - | - | $v_sC = C - C + vC - O + 6 + vC_4 - S + \delta_sCF_3$ |
| | | | 1005 | 20 | | 1045 | 7 | 2 | | | | 1028(2) | 1023(15) | - | - | $v_{\rm s} C = C - C + 5 + vC_4 - S + \delta_{\rm s} CF_3$ |
| | | | 1035 | 26 | 2 | | | | 1008 | 13 | з | 1020(2) | 1016(10) 997(21) | _ | -1000(4) | $v_{s}C = C - C + v_{c} - O + 5 + v_{c} - 5 + \delta_{s}CF_{3}$ |
| | | | 957 | 78 | 1 | | | | 1000 | 15 | 5 | 889(4,br) | 890(22,br) | _ | - | yOH |
| | | | | | | 945 | 3 | 2 | | | | 877(6,br) | 880(16,br) | - | - | 9 + γOH |
| 0.44 | 50 | | | | | 941 | 72 | 1 | 000 | | | 877(6,br) | 880(16,br) | - | - | γOH + 9 |
| 941 037 | 53 26 | 1 | | | | | | | 933 | /1 | I | 877(6,br) | 880(16,br) 924(14) | - | - 024(6) | γOH 9 + vOH |
| 928 | 41 | 15 | 932 | 31 | 25 | | | | | | | 906(6) | 903(27) | 906(14) | 905(29) | $\delta CCC + 17$ |
| | | | 927 | 0 | 3 | | | | 926 | 4 | 7 | - `` | 918(11) | - ` ` | 916(7) | 9 |
| | | | | | | 919 | 18 | 12 | 922 | 8 | 13 | 911(1) | 910(8) | 908(10) | 912(10) | δCCC + 17 |
| 872 | 2 | 1 | 970 | 10 | G | 878 | 1 | 1 | 970 | 15 | 0 | 852(3) | 850(22) | 849(4) | 851(5) | 19 |
| 865 | 23 | 4 | 870 | 19 | 0 | 866 | 25 | 6 | 870 | 15 | 9 | 860(14) | 859(30) | 862(11) | 860(28) | 7 + 17 7 + 17 |
| 000 | 20 | - | 855 | 4 | 2 | 000 | 20 | 0 | 857 | 2 | 1 | 842(3) | 844(14) | 835(5) | 843(4) | 19 |
| | | | | | | 832 | 61 | 1 | 832 | 57 | 2 | 802(14)* | 811(38) | 804(3)+ | 809(6) | $\gamma CH_{\alpha} + 19$ |
| 818 | 58 | 1 | 817 | 59 | 1 | 704 | 11 | 2 | | | | 792(12) | 802(55) | 804(3)+ | 809(6) | $\gamma CH_{\alpha} + 19$ |
| 780 | q | 3 | | | | 794 | 11 | 2 | 781 | 23 | 2 | 787(6) 774(3) | 789(20) 776(17) | 785(8)+ 778(5)+ | 787(5) 779(7) | $o_{s}CF_{3} + \Delta + 18 + VC - CF_{3}$ $\delta_{s}CF_{2} + \Delta + 18 + VC - CF_{3}$ |
| , 30 | 5 | J | 769 | 9 | 3 | | | | /01 | 25 | 2 | 771(3) | 773(11) | 774(3)+ | 773(18) | $\delta_{\rm s} {\rm CF}_3 + \Delta + 18 + v {\rm C} - {\rm CF}_3$ |
| 762 | 2 | 0 | 762 | 12 | 1 | | | | | | | - * | - , | - | - | $\gamma CH_{\alpha} + \Gamma$ |
| 752 | 5 | 8 | | | | 752 | 4 | 9 | | | | 755(1) | 750(40) | 757(8)+ | 754(10) | 18 |
| | | | | | | 751 | 0 | 0 | | | | /55(1) | 750(40) | /5/(8)+ | /54(10) | $\gamma CH_{\alpha} + T + 20$ (Continued on next next) |
| | | | | | | | | | | | | | | | | (communed on next page) |

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Table 2 (continued)

| Theoretical | | | | | | | | | | | Experime | ental | | Assignment | | |
|-------------|--------------|----------------|------|--------------|-------------|------|--------------|-------------|------|--------------|----------------|------------------|----------|------------------|---------|--|
| A1 | | | A2 | | | B1 | | | B2 | | | IR | IR Raman | | | |
| Freq | $I_{\rm IR}$ | A _R | Freq | $I_{\rm IR}$ | $A_{\rm R}$ | Freq | $I_{\rm IR}$ | $A_{\rm R}$ | Freq | $I_{\rm IR}$ | A _R | CCl ₄ | Solid | CCl ₄ | Solid | |
| | | | | | | | | | 749 | 7 | 0 | 752(3)* | 746(58) | 751(16)+ | 750(25) | $18 + \gamma CH_{\alpha} + \Gamma + \delta_s CF_3$ |
| | | | | | | | | | 749 | 8 | 10 | 752(3) | 746(58) | 751(16)+ | 750(25) | $\gamma CH_{\alpha} + \Gamma + 18$ |
| | | | 749 | 11 | 12 | | | | | | | 752(3) | 746(58) | 751(16)+ | 750(25) | $18 + \delta_s CF_3$ |
| | | | | | | | | | 731 | 65 | 2 | 726(8) | 732(64) | 728(4)+ | 731(4) | $20 + \gamma CH_{\alpha}$ |
| 727 | 72 | 3 | 725 | 59 | 1 | 728 | 72 | 3 | | | | 719(66) | 726(39) | 719(7) | 723(5) | $20 + + \gamma CH_{\alpha}$ |
| 707 | 3 | 1 | 707 | 0 | 1 | 712 | 0 | 0 | 714 | 0 | 1 | 710(1) | 706(17) | 707(6) | 709(7) | Γ + 10 |
| 704 | 38 | 10 | | | | | | | | | | 695(3) | 694(8) | 696(8) | 692(9) | $8 + \delta_s CF_3 + \Delta$ |
| | | | 688 | 39 | 19 | 690 | 22 | 8 | | | | 681(4) | 681(36) | 680(25) | 681(56) | $8 + \delta_s CF_3 + \Delta$ |
| | | | | | | | | | 682 | 13 | 30 | 672(2) | 671(15) | 673(12) | 673(21) | $8 + \Delta + \delta_s CF_3$ |
| | | | | | | | | | 649 | 63 | 5 | 641(14) | 640(43) | 640(12) | 641(17) | $8 + \delta_s CF_3 + \Delta$ |
| | | | 644 | 40 | 10 | | | | | | | 634(1) | 632(14) | 636(9) | 637(14) | $8 + \Delta + \delta_s CF_3$ |
| 615 | 33 | 10 | | | | 615 | 40 | 5 | | | | 607(10) | 608(8) | 606(11) | 607(7) | $8 + \Delta + \delta_s CF_3$ |
| | | | | | | 580 | 10 | 1 | 579 | 11 | 1 | 580(11) | 584(22) | 586(5) | 584(8) | $\delta_3 CF_3 + \Delta$ |
| 574 | 19 | 1 | 573 | 19 | 2 | | | | | | | 578(8) | 578(10) | 579(6) | 575(6) | $\delta_3 CF_3 + \Delta$ |
| | | | | | | 571 | 1 | 0 | 571 | 1 | 0 | 563(1) | 563(9) | 562(6) | 563(9) | 11 |
| 569 | 1 | 0 | 568 | 1 | 0 | | | | | | | 558(1) | 558(12) | 555(5) | 559(7) | 11 |
| 514 | 2 | 1 | 514 | 2 | 1 | 515 | 1 | 1 | 515 | 1 | 2 | 518(1) | 517(7) | 518(7) | 515(9) | $\delta_{3}CF_{3} + \Gamma$ |
| | | | | | | | | | 480 | 3 | 9 | 470(1) | 471(11) | 471(10)* | 471(34) | $\Delta + \delta C$ -thio |
| | | | 465 | 4 | 2 | | | | | | | 461(3) | 458(18) | 457(10)* | 457(14) | <i>∧</i> + 21 |
| | | | 464 | 4 | 1 | | | | | | | 461(3) | 458(18) | 457(10) | 457(14) | 21 + 1 |
| | | | | - | - | 461 | 3 | 2 | 464 | 3 | 1 | 461(3) | 458(18) | 457(10) | 457(14) | 21 |
| 462 | 3 | 1 | | | | 101 | 5 | - | | 5 | • | 461(3) | 458(18) | $457(10)^{*}$ | 457(14) | 21 + Γ |
| 102 | 5 | • | | | | 458 | 9 | 13 | | | | 461(3) | 458(18) | $457(10)_{*}$ | 457(14) | $4 \pm \delta C$ = thio |
| 445 | 0 | 2 | | | | 150 | 5 | 15 | | | | 434(2) | 434(3) | 433(10) | 430(9) | $\delta C_{-thio} + \delta_{-} CE_{o}$ |
| 443 | 0 | 0 | 447 | 0 | 1 | | | | | | | 434(2) | 434(3) | 433(10) | 430(9) | $\delta_a CE_a + \delta C - CE_a + A$ |
| | U | U | 112 | U | 1 | 437 | 2 | 0 | 434 | 2 | 1 | 434(2) | 434(3) | 433(10) | 430(9) | $\delta CE_{a} + \delta C - CE_{a} + A$ |
| | | | | | | 360 | 1 | 1 | 151 | 2 | • | 131(2) | 131(3) | 135(10) | 130(3) | A |
| 353 | 3 | 1 | 355 | 3 | 1 | 500 | 1 | 1 | | | | 354(1) | 355(2) | 345(8) | 346(10) | 4 |
| 555 | 5 | 1 | 555 | 5 | 1 | | | | 346 | 0 | 2 | 3/8(1) | 3/8(1) | 330(7) | 340(0) | 4 |
| 325 | 3 | 1 | | | | | | | 540 | 0 | 2 | 304(3) | 305(7) | 304(11) | 303(27) | $\nu \Omega = 0 + \alpha C F_{\tau}$ |
| 525 | J | 1 | 216 | 4 | 1 | 212 | 4 | 4 | 212 | 0 | 2 | 204(3) | 202(1) | 204(11) | 207(27) | p = p = 1 |
| | | | 510 | 4 | 1 | 202 | - | 4 | 204 | 0 | 1 | 234(1) | 233(4) | 235(13) | 237(23) | $\pi CE + \Gamma$ |
| 205 | 0 | 0 | 205 | 1 | 0 | 502 | 0 | U | 504 | 0 | 1 | _ | _ | _ | _ | $\pi C F_3 + \Gamma$ |
| 205 | 2 | 6 | 265 | 1 | 0 | 242 | 1 | 1 | | | | - | - | - | - | ACI'3 + 1 |
| 243 | 2 | U | 222 | 1 | 7 | 245 | 1 | 1 | 224 | 2 | 1 | 241(1) 224(2) | 234(0) | 239(20) | 235(27) | |
| 220 | 1 | 2 | 232 | 1 | 2 | | | | 234 | 2 | 1 | 234(3) | 229(4) | 232(20) | 233(23) | Δ π thio + Γ |
| 220 | 1 | 2 | 221 | 1 | 2 | 107 | 0 | 4 | 201 | 0 | 4 | 210(2) | 223(2) | 223(20) | 222(23) | π thio + Γ |
| 100 | 1 | 2 | 101 | 2 | 1 | 197 | 0 | 4 | 201 | 0 | 4 | 206(2) | 208(4) | 208(38) | 210(39) | $\pi \lim_{t \to \infty} + i C$ |
| 196 | 1 | 2 | 191 | 2 | 1 | 197 | 3 | 1 | 191 | 3 | 1 | 195(3) | 197(6) | n.m. | 198(34) | $\rho \text{time} + \delta \text{C} - \text{C} \text{F}_3$ |
| 100 | | | 110 | | 4 | 129 | 3 | 1 | 131 | 3 | 1 | 138(3) | 139(15) | n.m. | - | $\gamma C - CF_3 + I$ |
| 109 | 1 | 1 | 110 | 1 | 1 | | | | | | | n.c. | 108(3) | n.m. | 101 | $\gamma C - C F_3 + I$ |
| 97 | 0 | I | 94 | 0 | I | | 0 | 0 | | 0 | 0 | n.c. | 73(13) | n.m. | /1 | 1 |
| 0.2 | 0 | 0 | 07 | 0 | 0 | 88 | 0 | 0 | 84 | 0 | 0 | n.c. | n.c. | n.m. | - | I SC C this t |
| 83 | 0 | 0 | 87 | 0 | 0 | 81 | 0 | 0 | 84 | 0 | 1 | n.c. | n.c. | n.m. | - | $\partial C_{\alpha} - C - \text{tnio} + \Delta$ |
| 36 | 1 | 6 | 35 | 0 | 4 | 39 | 1 | 6 | 41 | 0 | 4 | n.m. | n.m. | n.m. | 3/ | τιπιο |
| 24 | 0 | I | 22 | 0 | 2 | 20 | 0 | 1 | 18 | 0 | 2 | n.m. | n.m. | n.m. | n.m. | τ CF ₃ |

^a Freq, vibrational wavenumber (calculated at the B3LYP/6-311G^{**} level); I_{IR} , IR intensities in kM/mol (calculated at the B3LYP/6-311G^{**} level); A_R , Raman activities in A^{**}4/ AMU (calculated at the B3LYP/6-31G^{**} level); experimental intensities are given in parenthesis; vbr, very broad; v, stretching; δ , in-plane bending; γ , out-of-plane bending; ρ , in-plane rocking; π , out-of-plane rocking; π , out-of-plane rocking; π , out-of-plane ring deformation; Γ , out-of-plane ring deformation; τ , torsion; n.c., not certain; n.m., not measured; thio, thienyl group; *, in CS₂ solution; +, in CH₃CN solution.

bands corresponding to these tautomers in the entire region of both Raman and IR spectra of TTFA. Upon deuteration, the bands at 3117 and 3108 cm⁻¹ disappear and a relatively weak band appears at 2322 cm⁻¹. Therefore we assigned these two bands to the CH_{α} stretching and the four other bands to the CH stretching modes of the thienyl group.

4.2.2. OH stretching mode

The position and the shape of the O–H stretching band are closely related to the shape of the potential energy function governing the motion of the proton. The enol form of β -diketones exhibits an extremely broad band in the 3500–2200 cm⁻¹ region of the IR spectrum, which upon deuteration of the enolic proton, appears as a new narrower but still broad band in the 2200–1800 cm⁻¹ region [16–20]. Because of the broadness and mixing with several combinations and overtones, and overall lose of their real spectral shapes, it is difficult to determine the center of these vOH and vOD bands (see Fig. 4). But deconvolutions of the infrared spectrum of TTFA solutions in CCl₄ and CS₂ in the 3000–2400 cm⁻¹ region display a broad band centered at 2850 cm^{-1} with a half width at half maximum (HWHM) of about 300 cm^{-1} , which is assigned to the OH stretching frequency. Deconvolution of the broad band in the $2300-1800 \text{ cm}^{-1}$ region in the IR spectrum of D₂-TTFA in the CCl₄ solution indicates a relatively narrower band centered at about 2080 cm^{-1} with a HWHM of about 200 cm^{-1} . These frequencies are considerably higher than those observed for AA/D₂-AA, $2750/2020 \text{ cm}^{-1}$ [16], but lower than those of TFAA/D₂-TFAA (1,1,1-trifluoroacetylacetone), $2900/2120 \text{ cm}^{-1}$ [16]. This indicates a weaker IHB and a stronger IHB for TTFA in comparison with those of AA and TFAA, respectively [24]. These results are in agreement with the ¹H NMR of these compounds, which reports the proton chemical shifts for AA, TTFA, and TFAA as 15.4, 14.9, and 14.2 ppm (all in CCl₄ solution), respectively [34].

4.2.3. 1700–1000 cm⁻¹ region

Beside the C–C stretching and C–H bending modes of the thienyl ring and CF_3 stretching modes, five bands are expected to be observed in this region related to the vibrations of the chelated

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Table 3 Fundamental band assignment of D_2 -TTFA (frequencies in cm⁻¹).^a

| Theoret | ical | | | | | | | | | | | Experimen | tal | | | Assignment |
|--------------|--------------|----------------|----------------------|--------------|-----------------|----------------------|--------------|----------------|----------------------|--------------|-----------------|--|--|--|--|---|
| A1 | | | A2 | | | B1 | | | B2 | | | IR | | Raman | | |
| Freq | $I_{\rm IR}$ | A _R | Freq | $I_{\rm IR}$ | A _R | Freq | $I_{\rm IR}$ | A _R | Freq | $I_{\rm IR}$ | A _R | CCl ₄ | Solid | CCl ₄ | Solid | |
| 3246 3231 | 1 1 | 209 92 | 3244 | 1 | 216 | 3244 3228 | 0 1 | 211 90 | 3242 | 1 | 212 | 3114(2) 3103(1) | 3113(18) 3104(12) | 3112(11) 3104(6) | 3116(15) 3100(9) | 1 2 |
| 3211 | 4 | 145 | 3221 3208 2405 | 2 4 2 | 108 83 11 | 3209 | 4 | 136 | 3219 3206 2404 | 2 5 3 | 109 87 11 | 3096(1) 3084(1) 2314(2) | 3094(13) 3086(12) 2318(9) | 3096(5) 3084(4) 2322(2) | 3094(12) 3085(8) 2318(3) | 2 13 vCD |
| 2396 2247 | 5 247 | 11 5 | 2218 | 263 | 5 | 2393 2237 1664 | 2 215 | 11 24 17 | 2249 | 214 | 29 | 2314 2080(2) 1624(28) | 2318 2090(4) 1627(61) | 2322 | 2318 | vCD vOD |
| 1659 | 133 | 19 | 1651 | 161 | 37 | 1004 | 432 | 17 | 1001 | 202 | 17 | 1626(40) 1621(34) | 1629(50) 1623(62) | 1627(8) 1617(10) | 1628(6) 1618(7) | $v_a C = C - C = 0$ $v_a C = C - C = 0$ $v_a C = C - C = 0$ |
| 1574 | 526 | 471 | 1574 | 303 | 369 | 1579 | 84 | 199 | 1581 | 39 | 428 | 1563(20) 1539(47) | 1560(40) 1534(42) | 1561(29) 1537(51) | 1555(30) 1534(37) | $v_{s}O=C-C=C+14 + vC-CF_{3} + \delta OD$ $v_{s}C=C-C=O+14 + vC-thio$ |
| 1526 | 599 | 107 | 1530 | 761 | 178 | 1558 | 84 | 253 | 1559 | 46 | 68 | 1520(23) 1498(21) 1490(19) | 1522(36) 1500(20) 1491(21) | 1519(25) 1494(11) 1487(10) | 1522(23) 1500(11) 1486(8) | $14 + v_{s}(C=0, C-0) + v_{a}C-C=C + vC-CF_{3}$ $v_{a}C=C-C + vC-0 + \delta OD + 14$ $v_{c}C=C-C + vC-0 + \delta OD + 14$ |
| 1462 | 93 | 700 | 1457 | 65 | 743 | 1457 | 109 | 367 | 1456 | 119 | 385 | 1419(28) 1411(31) 1411(31) | 1428(39) 1419(48) 1419(48) | 1420(38) 1417(100) 1417(100) | 1422(30) 1416(100) 1416(100) | 3 + vC - thio + vC - O $3 + vC - thio + vC - O$ $3 + vC - thio + vC - O$ $3 + vC - o + vC - thio$ |
| 1.410 | -7 | 22 | 1420 | 46 | 2 | 1429 | 35 | 29 | 1428 | 58 | 22 | 1407(26) 1398(16) | 1407(47) 1398(41) | 1410(64) 1399(17) | 1409(50) 1396(19) | $v_{a}C-C=C-0 + vC=0 + 3 + vC-CF_{3}$ 4 + $v_{a}(C-0,C=0)$ |
| 1412 1394 | 16 | 82 | 1394 | 45 | 116 | 1387 | 273 | 47 | 1384 | 50 | 19 | 1390(12) 1363(15) 1356(23) 1356(23) | 1389(29) 1366(20) 1357(45) 1357(45) | 1362(9) 1354(14) 1354(14) | 1383(12) 1359(11) 1354(20) 1354(20) | $v_a \cup -t = t - t$ $4 + v_a \cup -t = t - C$ $4 + v_C - C = C - C + vC - CF_3 + vC - thio + \delta OD$ 4 + vC - O 4 |
| 1351 | 55 | 1 | 1353 | 21 | 4 | | | | 1332 | 625 | 4 | 1332(17) 1332(17) 1313(41) | 1333(44) 1333(44) 1314(62) | - - 1312(7) | - - 1315(6) | $4 + v_{s}O-C=C-C + vC-CF_{3}$ $4 + vC-CF_{3} + v_{s}C=C-C$ $vC-C + vC-CF_{3} + vC-thio$ |
| | | | 1253 | 5 | 4 | 1314 | 527 | 17 | 1258 | 1 | 7 | 1281(29) 1253(25) - | 1289(55) 1261(49) - | 1278(13) 1252(8) 1244(8) | 1282(8) - 1244(7) | $vC-C + vC-CF_3 + vC-thio$ 15 15 + $vC-O$ |
| 1252 | 60 | 7 | | | | 1245 | 83 | 7 | | | | 1232(24) 1217(32) | 1239(42) 1225(67) | 1232(6) 1220(4) | 1238(6) | $15 + v_{s}CF_{3}$ $15 + vC-CF_{3}$ |
| 1203 | 393 | 5 | 1221 | 528 | 10 | 1202 1195 | 93 266 | 8 0 | 1217 | 254 | 2 | 1113(29) 1113(29) 1191(49) 1191(49) | 1112(62) 1112(62) 1188(94) 1188(94) | 1111(5) 1111(5) 1187(4) 1187(4) | - - 1193(5) 1193(5) | $v_{s}CF_{3} + vC_{4} - S + v_{a}C = C - C + \delta OD + \delta CD$ $v_{s}CF_{3} + vC_{4} - S + vC - O + \delta CD$ $v_{a}CF_{3} + vC_{4} - S$ $v - CF_{a}$ |
| 1188 | 223 | 9 | 1188 | 256 | 1 | 1171 | 288 | 4 | 1171 | 289 | 4 | 1203(100) 1164(89) | 1200(100) 1155(87) | 1198(4) 1167(3) | 1206(5) 1164(5) | $v_a CF_3$ $v_a CF_3$ $v_a CF_3$ |
| 1169 | 41 | 12 14 | 1169 | 284 31 | 3 | 1124 | 94 | 44 | 1123 | 111 | 44 | 1091(8) 1091(8) | 1092(38) 1085(28) | 1083(20) 1083(20) | 1095(13) 1084(23) | $v_a C F_3$ 5 + $\delta O D$ 5 + $\delta O D$ |
| 1103 | 9 | 30 | 1101 | 4 | 40 | 1102 | 33 | 30 | 1104 1079 | 38 127 | 44 34 | 1075(7) 1051(14) 1045(19) | 1072(20) 1055(37) 1050(41) | 1075(16) 1049(14) 1042(19) | 1075(20) 1053(29) 1047(25) | $16 + \delta OD$ $\delta OD + 6$ $\delta OD + 6$ |
| 1068 | 30 | 45 | 1075 | 05 | 07 | 1064 | 148 | 16 | | | | 1040(17) 1040(17) | 1042(36) 1042(36) | 1042(13) 1038(14) 1038(14) | 1039(10) 1039(10) | $\delta OD + 6$ $\delta OD + 6 + v_s C = C - C$ |
| 1046 | 125 | 1 | | | | 1042 | 24 | 0 | | | | 1032(15) 1024(11) | 1028(25) 1025(24) | _ | _ | $6 + v_{s}C = C - C + vC_{4} - S + \delta_{s}CF_{3} + vC - O$ $5 + v_{s}C = C - C + vC_{4} - S + \delta_{s}CF_{3} + vC - O$ |
| | | | 1039 | 76 | 0 | 945 | 1 | 2 | 1016 | 22 | 1 | 1018(8) 996(7) - | 1015(22) 993(26) 935(3) | - - 935(2) | - 998(6) 933(2) | $v_{s}C = C - C + 5 + \nu C_{4} - S + \delta_{s}CF_{3} + \nu C - 0$ $v_{s}C = C - C + 5 + \nu C_{4} - S + \delta_{s}CF_{3} + \nu C - 0$ 9 |
| 938 897 | 0 24 | 3 13 | 927 | 0 | 3 | | | | 926 | 0 | 2 | - - 891(3) | 923(4) 918(5) 889(14) | 921(2) 921(2) 893(6) | 924(2) 919(2) 890 (7) | 9 9 δCD + Δ |
| 889 | 20 | 2 | 894 | 24 | 25 | 896 | 9 | 0 | 002 | 1 | 0 | 891(3) 881(5) 801(2) | 889(14) 870(16) | 893(6) 873(6) | 890 (7) 873(18) | δ CD + 17 δ CCC + 17 + δ OD |
| | | | 882 | 14 | 8 | 872 | 4 | 2 | 870 | 12 | 8 | 891(3) 891(3) 855(10) | 889(14) 889(14) 861(22) | 893(6) 853(7) | 890 (7) 890 (7) 855(9) | $\frac{\partial CD + 17}{\partial CD + 17 + \Delta}$ $\frac{\partial CCC + 17 + \Delta}{\partial OD}$ |
| 863 | 31 | 4 | 863 | 21 | 1 | 858 | 40 | 10 | | | | 844(6) 844(6) 844(6) | 850(30) 850(30) 850(30) | 842(9) 842(9) 842(9) | 841(13) 841(13) 841(13) | $7 + 17 + \delta CD$ $7 + 17 + \Delta$ $7 + \delta CCC + \delta OD$ |
| 872 | 2 | 1 | 856 | 1 | 2 | 878 | 1 | 1 | 858 856 | 0 26 | 1 5 | 839(3) 839(3) | 842(17) 842(17) | 835(7) 835(7) | 843(11) 843(11) | $19 \\ 7 + \delta CD + \delta OD$ |
| 804 | 56 | 1 | 803 | 53 | 0 | 801 784 | 61 | 1 | 800 778 | 16 | 2 | sol. sol. | 807(27) 800(15) 775(34) | sol. sol. sol. | 814(4) 800(12) 773 (11) | $\Delta + vC - CF_3 + \delta_s CF_3$ 18 + $\Delta + vC - CF_3 + \delta_s CF_3$ |
| 763 751 | 12 | 3 | 760 | 5 | 4 | 750 | 4 | 0 | | | | sol. sol. | 769(23) 769(23) 746(63) | sol. sol. | 766(5) 766(5) 750(22) | $17 + \varDelta + \nu C - CF_3 + \delta_s CF_3$ $18 + \varDelta + \nu C - CF_3 + \delta_s CF_3$ 18 |
| | Ŧ | 0 | 748 | 11 | 11 | 132 | 7 | 5 | 749 | 6 | 10 | sol. | 746(63) | sol. | 750(22) | $18 + \delta_{s}CF_{3}$ (Continued on next page) |

Table 3 (continued)

| Theoretical | | | | | | | | | | | Experim | ental | | Assignment | | |
|-------------|--------------|-------------|------|--------------|-------------|------|--------------|-------------|------|--------------|-------------|------------------|-------------|------------------|------------------|--|
| A1 | | | A2 | | | B1 | | | B2 | | | IR | | Raman | | |
| Freq | $I_{\rm IR}$ | $A_{\rm R}$ | Freq | $I_{\rm IR}$ | $A_{\rm R}$ | Freq | $I_{\rm IR}$ | $A_{\rm R}$ | Freq | $I_{\rm IR}$ | $A_{\rm R}$ | CCl ₄ | Solid | CCl ₄ | Solid | |
| | | | | | | | | | 732 | 74 | 2 | sol. | 731(83) | sol. | 729(4) | 20 |
| 727 | 73 | 3 | 729 | 84 | 2 | 729 | 56 | 3 | | | | 721(45) | 725(57) | 721(9) | 723(2) | 20 |
| 715 | 0 | 1 | 714 | 0 | 0 | 715 | 7 | 0 | 718 | 1 | 1 | - | 706(19) | 707(8) | 706(5) | Γ + 10 |
| 700 | 34 | 12 | | | | | | | | | | 696(4) | _ | 696(6) | 691(5) | $\delta_{s}CF_{3} + 8 + \varDelta$ |
| | | | 687 | 36 | 19 | | | | | | | 680(6) | 677(31) | 677(19) | 680(27) | $8 + \delta_s CF_3 + \Delta$ |
| | | | 686 | 16 | 1 | | | | | | | 629(7) | 631(41) | 627(6) | 631(8) | $\gamma OD + \gamma CD$ |
| | | | | | | 680 | 18 | 9 | 677 | 10 | 30 | 675(4) | 667(14) | 670(13) | 675(40) | $8 + \Delta + \delta_s CF_3$ |
| 675 | 18 | 1 | | | | 677 | 19 | 1 | 672 | 20 | 1 | 629(7) | 631(41) | 627(6) | 631(8) | $\gamma OD + \gamma CD$ |
| | | | | | | | | | 641 | 63 | 3 | 638(9) | 639(40) | 638(7) | 637(8) | $8 + \delta_{\rm s} CF_3 + \Delta$ |
| | | | 635 | 40 | 9 | | | | | | | 635(9) | 636(45) | 634(6) | 637(8) | $8 + \delta_s CF_3 + \Delta$ |
| | | | | | | 614 | 42 | 5 | | | | 606(7) | 609(17) | 606(9) | 606(4) | $8 + \delta_s CF_3 + \Delta$ |
| 612 | 33 | 10 | | | | | | | | | | 606(7) | 609(17) | 606(9) | 606(4) | $8 + \Delta + \delta_{c}CF_{3}$ |
| | | | | | | 593 | 14 | 1 | | | | 573(10) | 571(42) | 572(7) | 569(5) | vCD + v OD + 11 |
| | | | | | | | | - | 588 | 16 | 0 | 573(10) | 571(42) | 572(7) | 569(5) | vCD |
| 587 | 12 | 0 | 585 | 14 | 0 | | | | | | - | 573(10) | 571(42) | 572(7) | 569(5) | $v_{CD} + 11$ |
| | | 0 | 000 | •• | Ū | 578 | 10 | 1 | 577 | 10 | 1 | 580(10) | 583(34) | 583(4) | 582(5) | $\delta_{\rm c} C E_{\rm p} + A$ |
| | | | | | | 570 | 10 | | 571 | 10 | 0 | 563(4) | 565(29) | 562(5) | 562(3) | 11 |
| 570 | 20 | 2 | 569 | 19 | 2 | | | | 571 | • | Ū | 577(11) | 578(40) | 502(3) 577(7) | 576(5) | $\delta_{\rm c} CE_{\rm a} + 4$ |
| 564 | 9 | 0 | 564 | 0 | 0 | 567 | 6 | 0 | | | | 558(3) | 558(33) | 555(4) | 559(5) | $11 + \gamma CD$ |
| 513 | 1 | 1 | 512 | 1 | 1 | 512 | 0 | 1 | 512 | 0 | 1 | 511(2) | 513(8) | 513(8) | 511(6) | $\delta CF_0 + \Gamma$ |
| 515 | 1 | 1 | 512 | 1 | 1 | 512 | U | 1 | 171 | 3 | 0 | 511(2) nm | A66(0) | 515(0) sol | A67(27) | $4 \pm \delta C$ this |
| 461 | 4 | 1 | 463 | 6 | 2 | 460 | 3 | 2 | 463 | 1 | 1 | n.m | 400(3) | sol. | 407(27) | 21 |
| 401 | 7 | 1 | 405 | 2 | 1 | 400 | 0 | 12 | 405 | 4 | 1 | n.m. | 455(25) | sol. | 455(0) | $4 \pm SC$ this |
| 120 | ٥ | 1 | 430 | 0 | 1 | 451 | 5 | 12 | | | | n.m. | 433(23) | sol. | 455(5) | $A + \delta C = \pm \delta C C C E$ |
| 439 | 1 | 1 | 450 | 0 | 1 | | | | | | | n.m | _ | sol. | | $\Delta + \delta_a C r_3 + \delta C - C r_3$ |
| 450 | 1 | 2 | | | | /21 | 2 | 0 | 427 | 1 | 1 | n.m. | - 420(5) | sol. | 127(5) | $\Delta + \delta C = t H \delta C$ |
| | | | 252 | 2 | 1 | 257 | 2 | 1 | 427 | 1 | 1 | n.m. | 430(3) | 501. col | 437(3) | $\Delta + \partial_a C \Gamma_3 + \partial C - C \Gamma_3$ |
| 247 | 4 | n | 552 | 2 | 1 | 557 | 1 | 1 | 242 | 1 | 1 | 11.111. n.m. | 343(2) | sol. | 225(0) 225(C) | 4 |
| 220 | 4 | 2 | | | | | | | 542 | 1 | 1 | 11.111. | 207(11) | SOI. | 202(0) | |
| 320 | 3 | 0 | 207 | 4 | 1 | 202 | 4 | 4 | 202 | 0 | 4 | II.III. | 297(11) | SOI. | 298(20) | $v_0 = 0 + z_0^2$ |
| | | | 307 | 4 | 1 | 303 | 4 | 4 | 303 | 9 | 4 | 11.111. | 290(9) | SOI. | 289(13) | $VOO + \rho CF_3$ |
| 202 | • | 0 | 202 | | 0 | 299 | 0 | 0 | 300 | U | 1 | n.m. | _ | SOI. | _ | $\pi CF_3 + I$ |
| 282 | 0 | 0 | 283 | 1 | 0 | 2.40 | | | | | | n.m. | _ | SOI. | - | $\pi CF_3 + I$ |
| 241 | 3 | 6 | | | _ | 240 | I | I | | | | n.m. | - | sol. | 235(18) | Δ |
| 210 | | | 230 | 1 | 7 | | | | 232 | 3 | 1 | n.m. | n.m. | sol. | 231(14) | |
| 218 | I | 3 | 219 | I | 3 | | | | | | | n.m. | n.m. | sol. | 220(15) | π thio + I |
| | | | | | _ | 196 | 0 | 4 | 199 | 0 | 4 | n.m. | | sol. | 207(24) | π thio + I |
| 194 | 1 | 2 | 190 | 2 | 1 | 195 | 3 | 1 | 190 | 3 | 1 | n.m. | n.m. | sol. | 191(24) | ρ thio + $\delta C - CF_3$ |
| | | | | | | 126 | 3 | 1 | 128 | 3 | 0 | n.m. | n.m. | n.m. | n.m. | $\gamma C - CF_3 + \Gamma$ |
| 107 | 1 | 1 | 109 | 1 | 1 | | | | | | | n.m. | n.m. | n.m. | n.m. | $\gamma C - CF_3 + \Gamma$ |
| 94 | 0 | 1 | 92 | 0 | 2 | 86 | 0 | 0 | 82 | 0 | 1 | n.m. | n.m. | n.m. | n.m. | Γ |
| 83 | 0 | 0 | 86 | 0 | 0 | 81 | 0 | 0 | 84 | 0 | 0 | n.m. | n.m. | n.m. | n.m. | δC_{α} -C-thio + Δ |
| 36 | 1 | 6 | 35 | 0 | 4 | 39 | 1 | 6 | 41 | 0 | 4 | n.m. | n.m. | n.m. | n.m. | τthio |
| 24 | 0 | 1 | 22 | 0 | 2 | 20 | 0 | 1 | 18 | 0 | 2 | n.m. | n.m. | n.m. | n.m. | τCF_3 |

^a See footnotes of Table 2.



Fig. 4. The IR spectra of TTFA (-) and D2-TTFA (\cdots) in the OH/OD stretching region.

enol ring, which arise from the C–O, C=O, C–C, and C=C stretching and the O–H in-plane bending motions. In the C=O and C=C stretching region, with the exception of TFAA and HFAA

(1,1,1,5,5,5-hexafluoroacetylacetone), only one single band has apparently been observed in the IR spectra of the enol form of β diketones [18-23]. By deconvolution of the IR spectra of AA and its deuterated analogue, D₆AA, it was shown that another strong and broad band, corresponding to the very strong and relatively broad Raman band, lies under this band at the lower frequency side [12]. In the case of AA, these bands appear at 1642 and 1624 cm^{-1} in the gas phase and are shifted downward in the condensed phases [12]. Considering the vibrational behavior of other β-diketones, and with respect to the IR and Raman studies for thiophene by Pasterny [62], and also according to the calculated normal mode's frequencies of TTFA, we expect to observe three bands in the 1650–1500 cm⁻¹ region due to the asymmetric and symmetric C=C-C=O stretching and v14 (see Fig. 9) of the thienyl group. The deconvoluted IR and Raman spectra of TTFA in this region indicate existence of eight bands in this region with considerable intensities in either the Raman or IR spectra. As previously explained, the existence of these additional bands can be attributed to all four stable conformations of TTFA being present in comparable amounts in the sample. Considering the calculated results, the first three bands of the mentioned eight observed bands in the double bond region, which occur at 1651, 1636, and 1623 cm⁻¹, are attributed to the

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Fig. 5. The IR spectra of TTFA (-) and D2-TTFA (\cdots) in CCl₄ solution.



Fig. 6. The Raman spectra of TTFA (–) and D2-TTFA (…) in solid states.

 $v_aC=C-C=0$ coupled to the OH bending movement in B1 and B2, in A1, and in A2 conformations, respectively. Upon deuteration, these IR strong bands move downward to 1634, 1626, and 1621 cm⁻¹, which are in agreement with the calculated results and support the assignment. The next two bands at 1601 and 1583 cm⁻¹ with strong IR and Raman intensities, are assigned to the symmetric C=C-C=O stretching strongly coupled to the OH in-plane bending for A and B tautomers, respectively. Upon deuteration these bands shift downward to 1539 and 1563 cm⁻¹ and become strongly perturbed by the thienyl v14 vibrational mode. These five assigned bands are of special interest because in all IR and Raman spectra collected in the solid state, the intensities of the bands related to the B2 conformer dominate those of the other conformers. Contrarily, in the solutions, the intensities of bands for the A conformers are stronger than those of the B conformers (see Fig. 7). This means that in the solid state the major content of the sample is in the B2 form and in the solution states the A forms have more significant amounts. This result is in good agreement with the experimental X-ray results [50] in the solid state and the theoretical calculations in solution.



Fig. 7. The IR spectra of TTFA in CCl_4 (–) and TTFA in solid state (–).



Fig. 8. The deconvoluted IR spectrum of TTFA in CCl₄ solution.

The last bands of this group are at 1522, 1519, and 1508 cm⁻¹, which are assigned to the v14 of the thienyl group in the different conformers. According to the calculations, upon deuteration this vibration is strongly coupled to $v_sC=C-C=O$ and shifts toward higher frequencies.

According to the calculations and the experimental Raman spectrum of thiophene [62], the strongest Raman band at about 1410 cm^{-1} , which upon deconvolution indicates two bands at $1412 \text{ and } 1410 \text{ cm}^{-1}$, is assigned to the symmetric C=C-C=C stretching of the thienyl group, v3, in the different conformers.

Three relatively weak and broad bands are observed at 1456, 1448, and 1437 cm⁻¹. The first two bands are assigned to the asymmetric C–C=C–O stretching, coupled to δ OH, for A1 and A2 conformers, respectively, and the latter is the corresponding band for the B1 and B2 conformers. Upon deuteration, these bands shift about 50 cm⁻¹ towards lower frequencies which is in agreement with the theoretical results.

The relatively strong bands at 1356 and 1353 cm⁻¹ are assigned to the *v*4 vibrational mode of the thienyl ring.

Deconvolution shows other relatively strong bands at 1283, 1279, and 1274 cm^{-1} , which are attributed to the OH in-plane



Fig. 9. Characterization of the ring vibrational modes of thiophene molecule, obtained at B3LYP/6-311G** level of calculation.

bending modes of the A1 and A2 conformers, B2 conformer, and B1 conformer, respectively. This vibrational mode is strongly coupled to some other motions like C=C, C-thio, and C-CF₃ stretching movements and v15 of the thienyl group. The coupling with the C=C stretching explains the strength of the bands in the Raman spectrum. Upon deuteration these bands disappear and three relatively strong bands appear at 1051, 1045, and 1040 cm⁻¹ for D₂-TTFA, which is attributed to the OD in-plane bending coupled to the v6 of the thienyl group. The corresponding bands in AA/D₂-AA appear at 1298/1081 cm⁻¹. The considerably lower frequency of this mode in D₂-TTFA compared to that in D₂-AA is partly due to a weaker hydrogen bond in TTFA compared to that in AA.

Four relatively strong IR bands are observed at 1252, 1244, 1231, and 1222 cm⁻¹. The first is assigned to v15 for all four conformations coupled strongly to the C–thio stretching. The 1244 and 1222 cm⁻¹ bands are assigned to v15 coupled mainly to C4–S stretching for B2 and B1, respectively. The band at 1231 cm⁻¹ is the corresponding band for the A conformers. Upon deuteration these bands become less mixed and lose their Raman intensities, without any significant frequency shift, which is in good agreement with the calculated results.

The deconvoluted IR spectrum of TTFA shows four very strong bands at 1205, 1199, 1165, and 1162 cm⁻¹. According to the calculated results, these bands arise from pure asymmetric CF₃ stretch-

ing of the molecule. The symmetric CF_3 stretching frequency, which is strongly coupled to the δCH_{α} , is observed at 1110 cm⁻¹. The corresponding CF_3 stretching bands in the IR spectrum of TFAA are observed at 1200, 1162, and 1109 cm⁻¹ [21], which are very close to those observed in the IR spectrum of TTFA.

The CH_{α} in-plane bending, which is strongly coupled to the v_sCF_3 and v6 of the thienyl ring, is observed at 1110 cm⁻¹. Upon deuteration this band moves downward to 891 cm⁻¹ for δ CD.

The 1084, 1065, 1063, and 1059 cm⁻¹ bands, which are medium intense in both IR and Raman spectra and sensitive to deuteration, are assigned to v5 and v6 of the thienyl group. Upon deuteration, these two nearly pure motions become strongly coupled to δ OD.

The medium and relatively weak bands at 1032, 1028, 1020, and 996 cm⁻¹ are assigned to the symmetric stretching of C=C_{α}-C segment that is coupled to the stretching of C4–S in thienyl ring and symmetric deformation of CF₃, for A1, B1, A2, and B2 conformers, respectively. The character and frequency of these motions are not affected by deuteration. This result is also consistent with the theoretical calculations and can be used as additional evidence for the existence of all four conformations in both solid and solution states.

4.2.4. Below 1000 cm⁻¹ region

Two bands at 911 and 906 cm^{-1} , which show medium intensities in both the IR and Raman spectra, are attributed to the

 $\delta C - C_{\alpha} - C$ coupled to the v17 of thienyl ring. As a result of deuteration, these bands disappear and two new bands are observed at 881 and 855 cm⁻¹, which is consistent with the theoretical calculations.

The relatively weak and broad bands at 889 and 877 cm⁻¹ in the IR spectrum of TTFA are assigned to the OH out-of-plane bending mode. For the deuterated analogue, D₂-TTFA, these bands disappear and a new band appears at about 629 cm⁻¹, which is assigned to δ OD coupled to δ CD. The corresponding band in the IR spectrum of AA/D2-AA appears at 957/707 cm⁻¹ [12], which suggests that the intramolecular hydrogen bond in AA is considerably stronger than that in TTFA.

The relatively strong IR bands at 802 and 792 cm⁻¹ are assigned to the out-of-plane bending mode of CH_{α} coupled to v19 of the thienyl group. Upon deuteration these bands disappear and a new band appears at 573 cm^{-1} .

According to the calculated results, the 304 and 294 cm⁻¹ bands are attributed to the O…O stretching mode. In AA, the O…O stretching appears at 366 cm^{-1} , which also supports a much stronger hydrogen bond in AA than in TTFA.

5. Conclusion

Among 40 possible conformers of TTFA, only four conformers have the chelated IHB. The stability calculations in different solutions confirm that the energy differences of these four conformers, which are negligible in the gas phases, increase in polar solvents. This is in such a way that the A forms become clearly more stable than the B forms and new trend of stabilities in solution phase is A2 > A1 > B2 > B1.

The theoretical frequency calculations for different conformers and the results of the experimental IR and Raman studies suggest that all four chelated forms coexist in the solid and solution states. However, in agreement with the theoretical stability calculations and X-ray experimental investigation, the vibrational spectroscopy analysis specify a more ratio of A forms in the solution phases, and a more ratio of B forms in the solid state in the sample.

A complete vibrational assignment of the TTFA is presented. The FTIR spectrum of the molecule shows a very broad absorption band in the 3000–2400 cm⁻¹ region centered at about 2850 cm⁻¹, which is attributed to vOH. By comparison of this frequency and vOD (about 2080 cm^{-1}) of TTFA with those of AA and TFAA, it is concluded that the IHB strength trend for these molecules is AA > TT-FA > TFAA. This is confirmed by the further comparison of some other vibrational frequencies.

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