

## SUPPLEMENTARY INFORMATION

### REVISITING PHOTOISOMERISATION IN FLUORINATED ANALOGS OF ACETYLACETONE TRAPPED IN CRYOGENIC MATRICES

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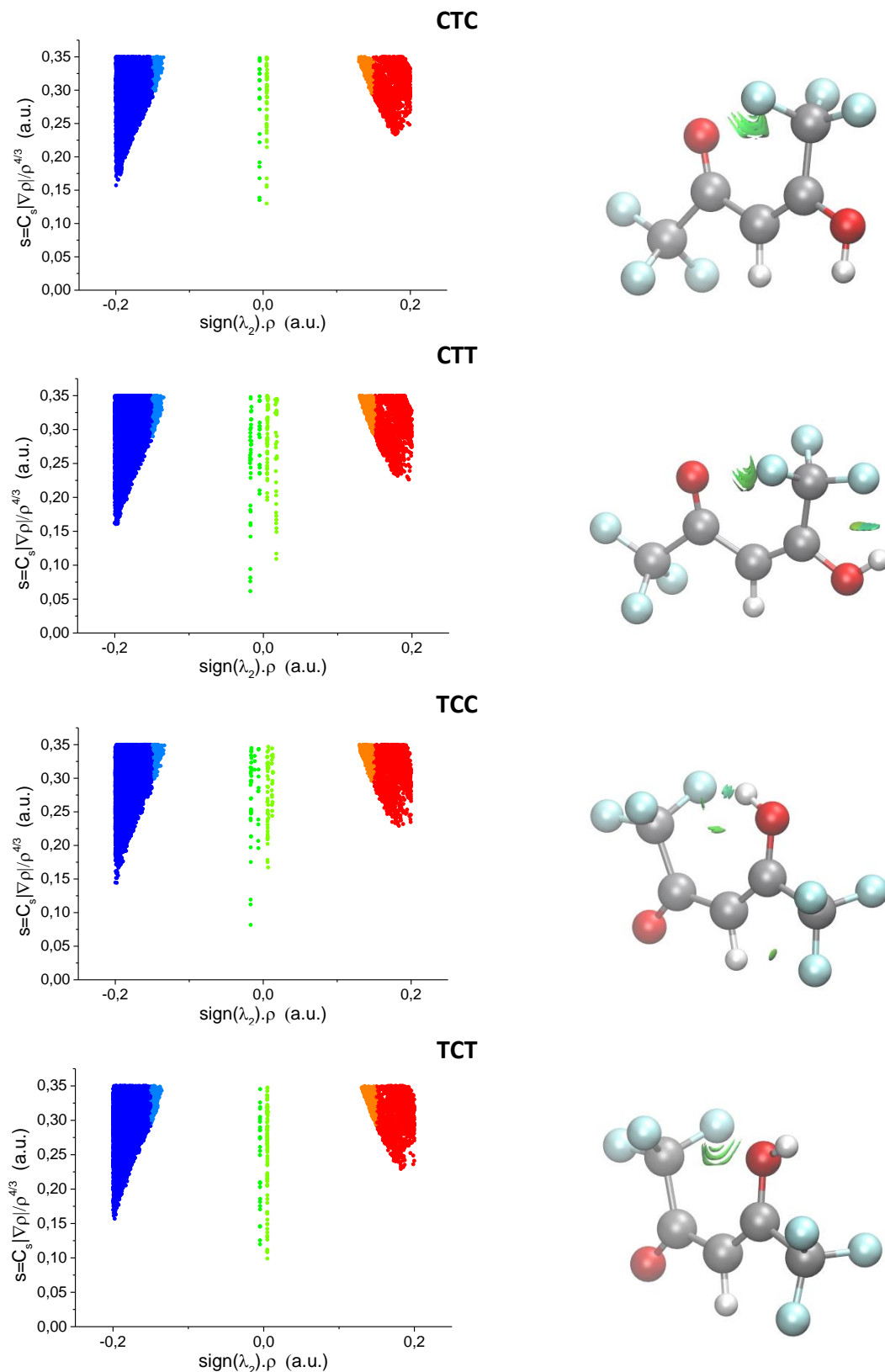
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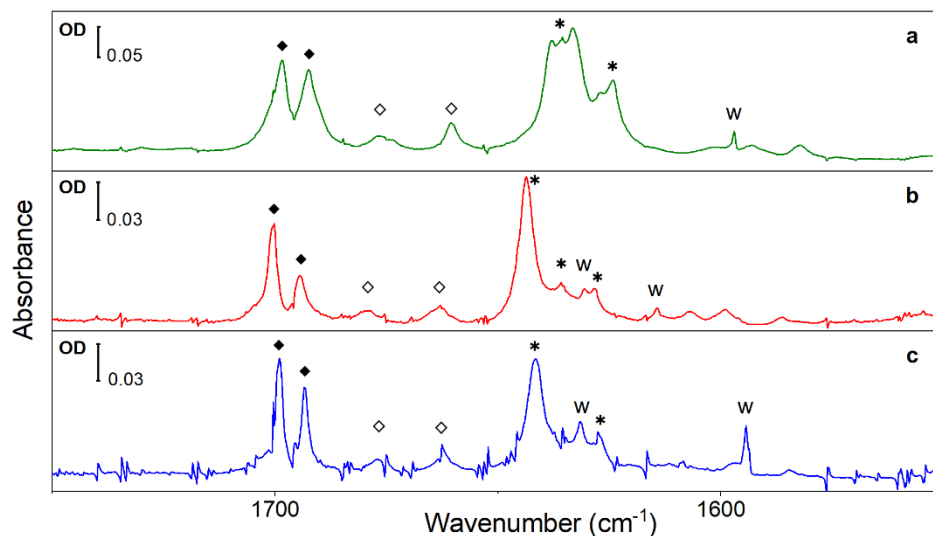
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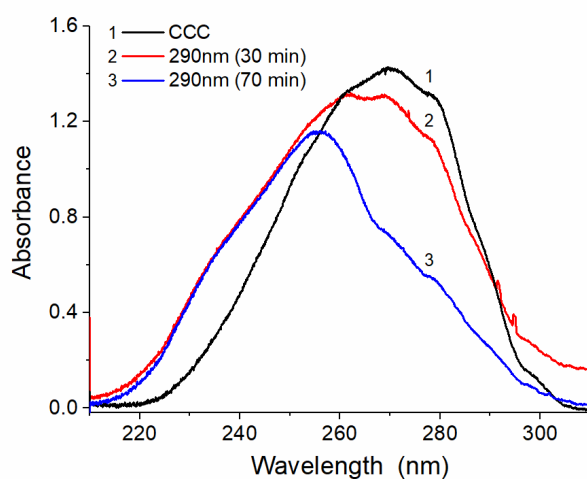
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**Fig. S1** Visualization of non-covalent interactions through NCI plot calculations for the CTC-CTT and TCC-TCT pairs. Left: Graph of reduced density gradient ( $s$ ) versus density multiplied by the sign of  $\lambda_2$  (second eigenvalue of the Hessian of the electronic density). Right: Isosurface of  $s$  at 0.35. The same color code is employed in the left and right panels: dark blue for strong attractive interactions, light green for weak interactions (either attractive or repulsive), and red for strong repulsive interactions. In the right panel, we observe the green color corresponding to steric repulsion, and an extra light blue-green region for CTC and TCC isomers corresponding to non-covalent interactions.

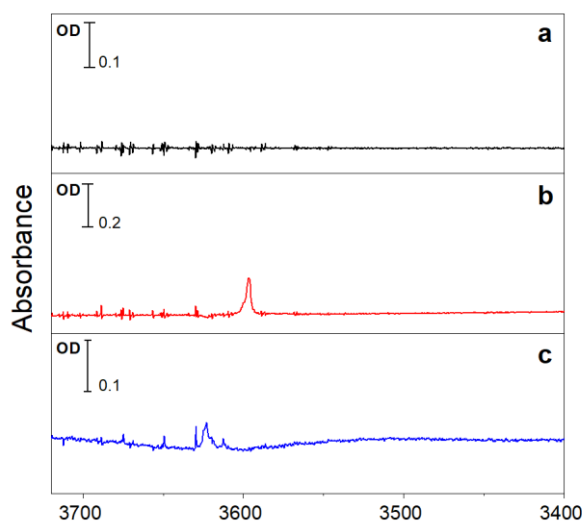




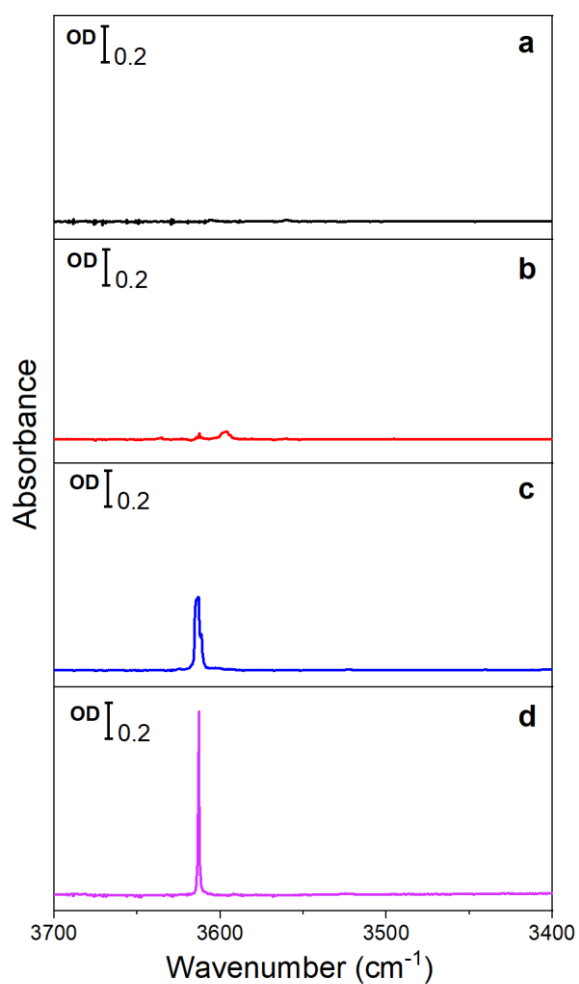
**Fig. S2** Expansion of Figure 3 in the 1750-1550  $\text{cm}^{-1}$  region in (a) nitrogen 3.2 K, (b) neon at 8 K and (c) *para*-hydrogen at 2.8 K. Two doublets appear in all the matrices near 1690  $\text{cm}^{-1}$  ( $\blacklozenge$ ) and 1670  $\text{cm}^{-1}$  ( $\diamond$ ). Multiplets are also observed in the band near 1640  $\text{cm}^{-1}$  (\*). Some experiments in nitrogen matrix have also been performed and are added in this graph to show the presence of the doublets. w: bands associated to water molecules trapped in the matrix.



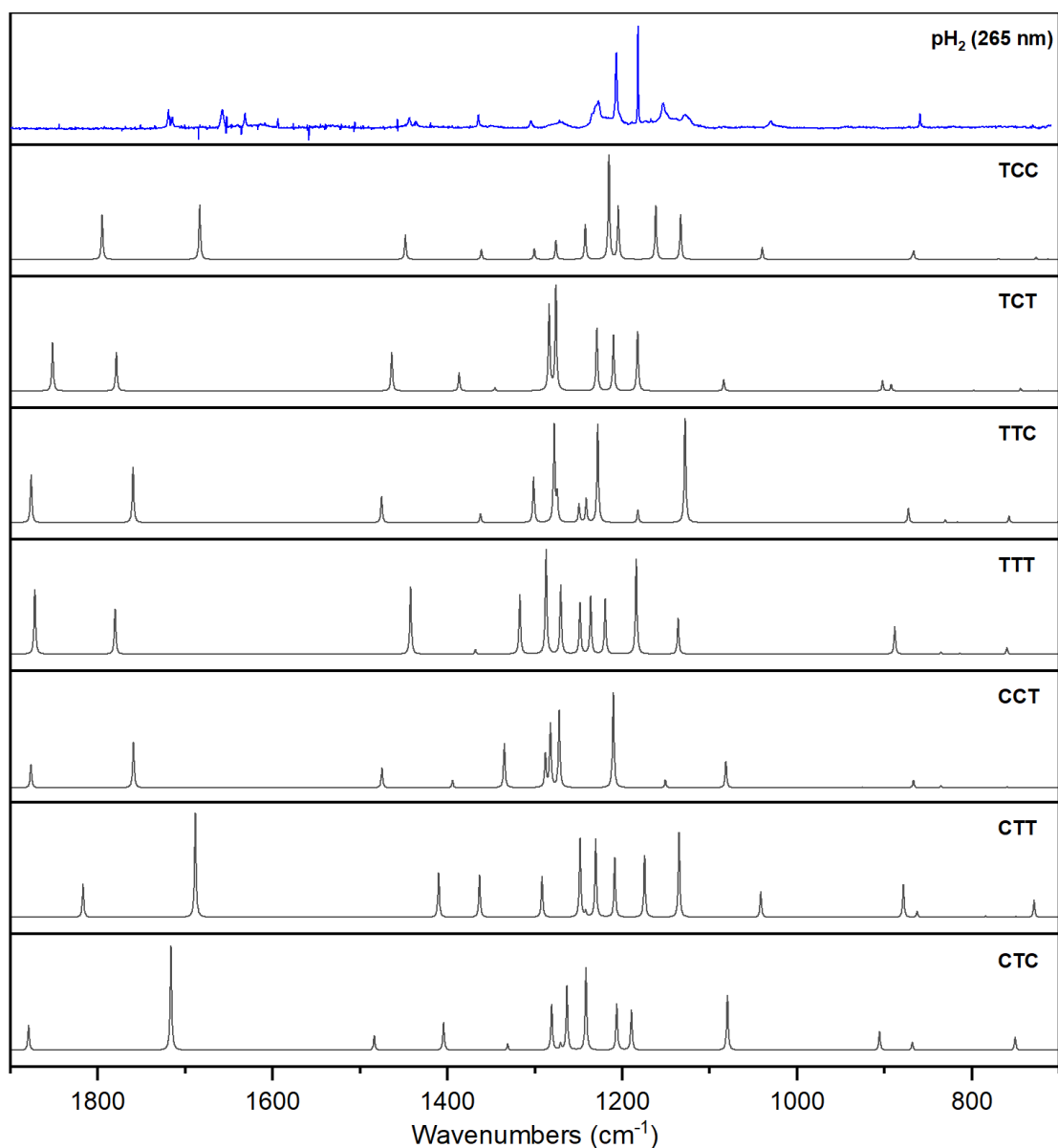
**Fig. S3** Electronic absorption spectra of hexafluoroacetylacetonide in neon matrix at 8 K. (1, black) deposited sample, (2, red) 30 min of irradiation at 290 nm (3, blue) 70 min of irradiation at 290 nm



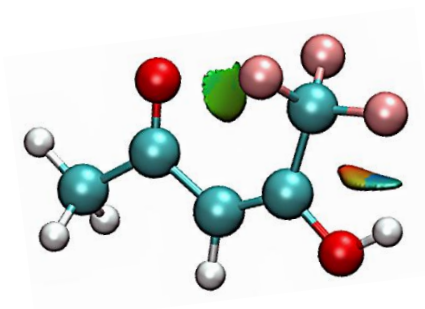
**Fig. S4** Infrared experimental spectra of hexafluoroacetylacetone in para-hydrogen matrix at 2.8 K. (a) as-deposited sample, CCC isomer, (b) CTT, and (c) TCC isomers



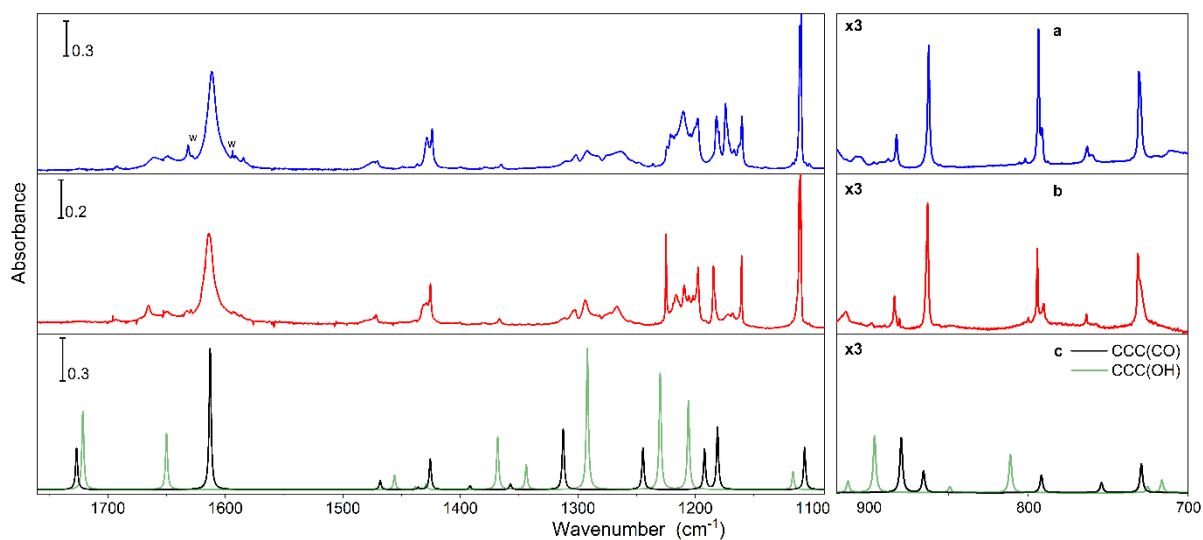
**Fig. S5** Infrared experimental spectra of trifluoroacetylacetone in para-hydrogen matrix at 2.8 K. (a) as-deposited sample, CCC, (b) CTC(CO), (c) CTT(OH), and (d) TCT(OH) isomers. The  $\nu_{\text{OH}}$  mode for the last two isomers is predicted to appear at very close frequencies (see Tables S7 and S8) as observed experimentally



**Fig. S6** Experimental infrared spectrum of TCC isomer of hexafluoroacetylacetonone in (a) neon matrix at 8 K after an irradiation of the deposited sample at 265nm. This spectrum is the result of subtractions of different spectra along irradiation to remove the CCC and CTT bands. The other panels show, as comparison, the simulated infrared spectra of all the open enol isomer. These spectra were obtained through frequency calculation of each optimized structure at the M06-2X/6a-311++G(3df,3pd) within the harmonic approximation. Frequency values in the figure are corrected with a 0.970 scaling factor, and each transition is represented by the convolution of a Lorentzian function (FWHM=2  $\text{cm}^{-1}$ ).



**Fig. S7** NCI calculation for the CTT(OH) conformer of trifluoroacetylacetone. Isosurface of the reduced density gradient ( $s$ ) at 0.35 value; light blue corresponds to attractive non-covalent interactions, while green and reddish colors correspond to repulsive interactions



**Fig. S8** FT-IR spectra deposited trifluoroacetylacetone in (a) para-hydrogen at 2.8 K and (b) neon matrices at 8 K, and (c) theoretical frequency calculation (M06-2X) of the two CCC tautomers in harmonic approximation with 0.973 scaling factor. (See ref. [1] for more details). The “Absorbance” axis in the right panel has been zoomed (x3) for a better comparison. w : bands associated to water molecules trapped in the matrix.

**Table S1:** Natural atomic charges for the oxygen atoms in H8-acac and F6-acac obtained by the NBO 3.0 module in Gaussian16 after optimization of the CCT isomer at M06-2X/6-311++G(3df,3pd).

	O (C=O)	O (O-H)
H8-acac	-0.567	-0.656
F6-acac	-0.487	-0.640

**Table S2:** Geometric parameters from the optimized geometries of the CCC conformer at M06-2X/6-311++G(3df,3pd). All the distances between two atoms are given in Ångströms (Å), and the angles in degrees (°)

Molecule	Distances					
	O····O	O-H	C=O	C-O	C=C	C-C
Acetylacetone	2.528	0.998	1.233	1.318	1.361	1.445
Trifluoroacetylacetone (CO)	2.584	0.986	1.221	1.315	1.364	1.430
Trifluoroacetylacetone (OH)	2.543	0.994	1.227	1.312	1.346	1.459
Hexafluoroacetylacetone	2.610	0.982	1.214	1.310	1.348	1.445
Molecule	Angles					
	O····H-O	O=C-C	C-C=C			
Acetylacetone	148.44	121.83	120.23			
Trifluoroacetylacetone (CO)	145.54	125.74	119.52			
Trifluoroacetylacetone (OH)	145.70	121.05	118.89			
Hexafluoroacetylacetone	142.02	124.96	118.32			

**Table S3:** Vibrational assignment of the CCC conformer of hexafluoroacetylacetone. Infrared experimental frequencies ( $\text{cm}^{-1}$ ) of the chelated enol form of AcAcF6 in nitrogen, neon and *para*-hydrogen matrices, and Raman experimental frequencies in argon matrix are compared to experimental values obtained in argon matrix [2]. Calculated harmonic frequencies [M06-2X/6-311++G(3df,3pd)] ( $\text{cm}^{-1}$ ) are also included for comparison. IR ( $\text{km/mol}$ ) intensities and Raman scattering activities ( $\text{\AA}^4/\text{amu}$ ) obtained in the harmonic approximation. Scaling factor (sf): 0.970

Assignment (simplified description)	Experimental						Theoretical		
	N <sub>2</sub>	Ne	pH <sub>2</sub>	Ar			Harmonic*sf	Int.	
				IR (this work)	Ref. [2] (IR)	Raman (this work)		IR	Raman
<b>vOH</b>							3353.2	206	43
<b>vCH</b>	3142.4	3148.7		3138.7			3171.0	11	40
	3123.4	3130.6	3126	3122.3		3125.9			
<b>vCO + vC=C (as)</b>	1698.7	1700.6	1699.0	1698.8	1699.0	1699	1753.2	151	16
	1692.6	1694.3	1693.4	1692.0		1692			
<b>vCO + vC=C (s) + <math>\delta</math>OH</b>	1637.9			1639.3		1639	1640.7	276	93
	1632.7	1643.7	1641.5	1629.4	1640.0	1634			
	1624.3			1623.8		1627			
						1612			
<b>vC-OH + <math>\delta</math>CH</b>	1441.9	1444.0	1442.5	1443.5	1445.0	1442	1456.2	128	7
<b><math>\delta</math>OH + vcarbon chain (as)</b>	1363.0	1366.9	1365.7	1363.7	1364.0	1363	1374.7	82	7
<b><math>\delta</math>OH + vcarbon chain (s)</b>	1288.8	1300.8	1298.8	1295.5	1296.0	1295	1305.0	89	15
<b><math>\delta</math>OH + vCF<sub>3</sub> (CO side) + C-CF<sub>3</sub> (OH)</b>	1267.6	1272.6	1271.7	1267.8	1269.0	1269	1270.7	536	4
				1264.4					
<b>vCF<sub>3</sub> (CO side)</b>	1225.5	1230.5	1229.3	1226.1	1227.0		1241.3	143	1
				1220.3					
<b>vCF<sub>3</sub> (OH side)</b>	1211.0	1219.7	1216.3	1216.6	1213.0	1211	1233.6	396	3
		1214.6	1212.3	1212.3					
<b>vCF<sub>3</sub> (OH side)</b>	1181.0	1191.1	1189.7	1183.5	1185.0	1183	1210.0	272	3
<b>vCF<sub>3</sub> (CO side)</b>	1165.4	1167.8	1166.8	1168.0	1168.0	1164	1185.6	259	1
				1162.6					
<b><math>\delta</math>CH</b>	1109.5	1111.1	1110.4	1109.9	1110.0	1110	1112.4	60	6
<b>vC-C</b>	1087.2	1090.6	1089.7	1089.1	1092.0	1087	1086.0	230	1



$\Delta$	915.5	917.9	917.2	917.4	918.0	916	911.2	12	10
$\Gamma$						823	823.4	70	1
$\delta_s\text{CF}_3$ (umbrella both sides) (as)	818.6	820.2	819.5	819.7	820.0	820	819.7	3	1
$\gamma\text{OH} + \gamma\text{CH}$	807.7	813.6	811.9			815	812.3	25	0.1
$\Gamma$	748.4	751.1	750.3	752.1	752.0	749	746.3	18	0.2
$\delta_s\text{CF}_3$ (umbrella both sides) (s)	741.4	742.4	742.5	742.7	744.0	741	739.9	14	8
$\Gamma$	716.6	717.5	717.4	717.4	719.0	716	714.0	12	0.4
$\delta_s\text{CF}_3$ (OH side)	658.5	660.1	659.8	659.8	660.0	659	651.4	61	0.2
$\delta_{as}\text{CF}_3$ (OH side)						585.7	578.6	23	1
$\delta_{as}\text{CF}_3$ (CO side)						573.3	565.8	13	0.1
$\delta_{as}\text{CF}_3$ (OH side) + $\delta_{as}\text{CF}_3$ (OH side)						525.5	518.5	3	1
$\delta_{as}\text{CF}_3$ (OH side) + $\delta_{as}\text{CF}_3$ (OH side)						512.7	505.0	0.3	1
$\delta_{as}\text{CF}_3$ (CO side)						438.2	430.9	0.2	2
$\delta_{as}\text{CF}_3$ (OH side)						432.1	424.3	1	0.5
$\delta\text{F-C-CO}$						355.6	348.9	1	1
$\Delta$						315.3	305.0	4	2
$\rho\text{CF}_3$ (OH side)						309.4	302.9	0.02	0.1
$\rho\text{CF}_3$ (CO side)						253.2	246.3	1	0.2
$\Delta$						236.5	228.8	2	2
$\pi\text{CF}_3$						219.7	211.1	4	1

$\nu$ , stretching;  $\delta$ , in plane bending;  $\gamma$ , out of plane bending;  $\rho$ , in plane rocking;  $\pi$ , out of plane rocking;  $\Delta$ , in plane ring deformation;  $\Gamma$ , out of plane ring deformation;  $s$ , symmetric;  $a$ , asymmetric

**Table S4** Vibrational assignment of the CTT isomer of hexafluoroacetylacetone. Infrared experimental frequencies ( $\text{cm}^{-1}$ ) in neon and *para*-hydrogen matrices. Calculated harmonic frequencies [M06-2X/6-311++G(3df,3pd)] ( $\text{cm}^{-1}$ ) are also included for comparison. IR ( $\text{km/mol}$ ) intensities were obtained in the harmonic approximation. Scaling factor (sf): 0.970. The mode assignments employed in ref. [2] do not exactly match those proposed in the present work.

Assignment (simplified description)	Frequencies			Theoretical Harmonic*sf	Infrared Intensities
	Experimental				
	Ar [2]	Ne	pH <sub>2</sub>		
vOH	3593	3612.8	3596.7	3732.5	261
vCH		3051.6	3048.8	3126.1	5
vC=O/vC=C (as)	1746	1751.7	1749.6	1816.7	124
vC=O/vC=C (s)/ $\delta$ OH	1663*	1663.6	1662.1	1688.3	387
$\delta$ OH/ $\delta$ CH	1410	1422.6	1421.8	1410.0	167
		1414.5	1413.6		
		1409.8	1410.0		
vC-OH/vC-CH <sub>3</sub>	1356*	1354.8	1354.5	1363.1	157
vCF <sub>3</sub> (CO side)/ $\delta$ OH/ $\delta$ CH	1290	1294.8	1289.1	1291.7	153
		1286.9			
vCF <sub>3</sub> (OH side)	1223*	1225.3	1224.0	1248.2	294
vCF <sub>3</sub> (both sides)/ $\delta$ OH/ $\delta$ CH	1237	1241.8	1241.0	1241.8	21
vCF <sub>3</sub> (CO side)/ $\delta$ OH/ $\delta$ CH	1206	1220.5	1217.8	1230.3	290
vCF <sub>3</sub> (OH side)/ $\delta$ CH	1193*	1193.5	1192.6	1208.4	221
vCF <sub>3</sub> (CO side)	1154	1157.1	1155.4	1174.4	231
vCF <sub>3</sub> (OH side)/ $\delta$ OH/ $\delta$ CH	1134*	1134.9	1135.4	1134.9	317
vC-C	1048	1047.8	1048.1	1041.5	97
vCF <sub>3</sub> (CO side)	881	880.0	879.5	878.4	123
$\gamma$ CH	855	855.5	856.9	862.7	23
$\delta_s$ CF <sub>3</sub> (OH side)	786	785.0	784.4	784.4	7
$\gamma$ CH/ $\gamma$ C=O	749	747.6	747.0	749.7	5
$\delta_s$ CF <sub>3</sub> (CO side)	734*	731.7	731.6	728.8	65
		730.2			
$\gamma$ CH/ $\Gamma$ (C=C-CF <sub>3</sub> )				686.1	2
$\Delta$				626.4	7
$\delta_{as}$ CF <sub>3</sub> (OH side)/ $\Delta$				573.8	1
$\delta_{as}$ CF <sub>3</sub> (CO side)/ $\Delta$				542.3	27
$\delta_{as}$ CF <sub>3</sub> (CO side)/ $\Gamma$				510.3	9
$\delta_{as}$ CF <sub>3</sub> (OH side)/ $\Gamma$				501.4	1
$\gamma$ OH				461.8	98
$\Delta$				439.6	2
$\Delta$				419.6	5
$\delta$ C-OH				372.3	5
$\delta$ C=O/ $\rho$ CF <sub>3</sub> (CO side)				315.4	5
$\gamma$ CH/ $\pi$ CF <sub>3</sub>				273.1	2
$\rho$ CF <sub>3</sub> (OH side)/ $\Delta$				268.4	6
$\pi$ CF <sub>3</sub> / $\Gamma$				235.9	0

$\Delta$	161.4	0.2
$\Gamma$	154.2	3
$\Delta$	111.4	0
$\Gamma$	92.7	0
$\tau\text{CF}_3(\text{CO side})/\Gamma$	33.8	0.8
$\Gamma$	20.2	0.0043

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$\nu$ , stretching;  $\delta$ , in plane bending;  $\gamma$ , out of plane bending;  $\rho$ , in plane rocking;  $\pi$ , out of plane rocking;  $\tau$ : torsion;  $\Delta$ , in plane ring deformation;  $\Gamma$ : out of plane carbon skeleton deformation; **s**, symmetric; **as**, antisymmetric. \* Bands exhibiting splitting in argon [2]. A grey background is used to identify multiplets

**Table S5** Vibrational assignment of the TCC isomer of hexafluoroacetylacetone. Infrared experimental frequencies ( $\text{cm}^{-1}$ ) in neon and *para*-hydrogen matrices. Calculated harmonic frequencies [M06-2X/6-311++G(3df,3pd)] ( $\text{cm}^{-1}$ ) are also included for comparison. IR ( $\text{km/mol}$ ) intensities were obtained in the harmonic approximation. Scaling factor (sf): 0.970

Assignment (simplified description)	Frequencies			Infrared Intensities
	Experimental		Theoretical Harmonic*sf	
	Ne	pH <sub>2</sub>		
vOH	3631.5	3623.7	3749.7	199
vCH	3234.4		3146.8	11
vCO	1722.1	1719.3 1714.4	1794.9	239
vC=C	1659.5	1658.0	1683.3	293
vC-OH	1445.0 1437.9	1443.5 1435.9	1448.0	134
vC-CH <sub>3</sub> /δCH	1365.4	1364.6	1361.0	56
vC-CH <sub>3</sub> /δOH/δCH	1306.0	1304.4	1300.5	59
vCF <sub>3</sub> (both sides)/δOH	1274.7	1272.3	1275.8	103
vCF <sub>3</sub> (both sides)/δOH	1235.4 1225.8 1219.9	1227.0	1242.2	188
vCF <sub>3</sub> (OH side)/δOH	1209.5	1206.8	1215.1	556
vCF <sub>3</sub> (OH side)	1184.0	1182.0	1204.4	283
vCF <sub>3</sub> (CO side)/δOH/δCH	1156.4	1153.1	1161.5	287
vCF <sub>3</sub> (CO side)/δOH/δCH	1119.1	1128.9	1133.1	239
vC-OH	1032.6	1030.3	1039.7	66
vC-CF <sub>3</sub>	858.4*	859.3*	868.3	17
γCH			866.5	44
δsCF <sub>3</sub> (CO side)	769.1		769.4	7
Γ(CO side)			734.0	1.3
δsCF <sub>3</sub> (OH side) /Δ	730.0	730.3	726.5	13
Γ(OH side)			712.8	3
Δ			645.2	35
δasCF <sub>3</sub> /Δ			575.7	0.2
δasCF <sub>3</sub> /Δ			548.3	23
δasCF <sub>3</sub> (OH side)/ Γ			522.6	13
δasCF <sub>3</sub> (CO side)/ Γ			506.7	0.1
δsCF <sub>3</sub> (CO side)/ γOH			457.4	8
γOH/ δsCF <sub>3</sub> (OH side)			436.1	17
γOH			401.7	28
Δ/δC=O			353.3	5
ρCF <sub>3</sub> (OH side)/δC-OH			314.4	2
γOH/πCF <sub>3</sub>			289.8	8
ρCF <sub>3</sub> (CO side)/Δ			260.9	4
πCF <sub>3</sub> (CO side)			229.3	2
Δ			183.8	4

$\Gamma$	135.5	3
$\Gamma$	123.0	2
$\tau\text{CF}_3(\text{CO side})$	78.8	2
$\tau\text{CF}_3$	41.7	1
$\tau\text{CF}_3(\text{OH side})/\Gamma$	28.9	0.1

$\nu$ , stretching;  $\delta$ , in plane bending;  $\gamma$ , out of plane bending;  $\rho$ , in plane rocking;  $\pi$ , out of plane rocking;  $\tau$ : torsion;  $\Delta$ , in plane ring deformation;  $\Gamma$ : out of plane carbon skeleton deformation; **s**, symmetric; **as**, antisymmetric. A grey background is used to identify multiplets. \* Two modes accidentally overlap in frequency and are assigned to the same experimental band

**Table S6** Vibrational assignment of the CTC(CO) isomer of trifluoroacetylacetone. Vibrational experimental frequencies ( $\text{cm}^{-1}$ ) in neon and *para*-hydrogen. Values for argon matrices from ref. [3] are also included. Calculated harmonic frequencies [M06-2X/6-311++G(3df,3pd)] ( $\text{cm}^{-1}$ ) are added for comparison. IR intensities ( $\text{km/mol}$ ) are obtained in the harmonic approximation. Scaling factor (sf): 0.973.

Assignments (simplified description)	Frequency			Theoretical	
	Ne	pH <sub>2</sub>	Ar [3]	Harm.*sf(0.973)	Infrared Int.
<b>vOH</b>	3614.8	3597.6	3588	3751.4	76
<b>vCH<sub>3</sub></b>	3022.0			3134.8	6
<b>vCH</b>	2967.0			3102.8	5
<b>vCH<sub>3</sub></b>	2932.0			3046.6	1
<b>vCH<sub>3</sub></b>				2990.5	4
<b>vC=O</b>	1732.2 1728.3	1730.9 1727.4	1725	1794.7	148
<b>vC=C</b>	1623.2 1616.3	1618.5	1617	1632.8	732
<b><math>\delta\text{CH}_3</math></b>				1451.0	10
<b><math>\delta\text{CH}_3/\delta\text{CH}/\delta\text{OH}/\text{vC-C}</math></b>	1448.4*	1447.3*	1447	1449.0	37
<b><math>\delta\text{CH}_3/\text{vC-CH}_3</math></b>	1428.4	1424.5		1425.3	32
<b><math>\delta\text{CH}_3/\text{vC-CF}_3</math></b>	1374.6	1372.4	1370	1369.2	81
<b>vC-CF<sub>3</sub>/<math>\delta\text{CH}_3</math></b>	1337.3 1331.9	1335.9 1330.2	1335	1339.4	134
<b>vCF<sub>3</sub>/<math>\delta\text{CH}</math></b>	1293.0	1292.3		1286.0	11
<b>vCF<sub>3</sub>/<math>\delta\text{CH}</math></b>	1221.5 1219.3	1221.3	1218	1235.9	213
<b><math>\delta\text{CH}/\delta\text{OH}</math></b>	1204.2 1197.8	1204.3 1197.7	1195	1196.6	119
<b>vCF<sub>3</sub></b>	1150.5	1149.0	1147	1170.7	262
<b>vC(H)-C(=O)/vC-CH<sub>3</sub>/ vCF<sub>3</sub></b>	1083.8	1084.0	1084	1082.9	225
<b><math>\rho\text{CH}_3</math></b>				1039.0	1
<b><math>\rho\text{CH}_3</math></b>	1016.6	1015.3	1014	1010.0	40
<b>vC-CF<sub>3</sub></b>	877.4	877.2	878	884.6	109
<b>vC-CH<sub>3</sub></b>	853.7	852.6		852.9	1
<b><math>\gamma\text{CH}</math></b>	817.9 814.1	817.7 815.0	815	824.4	53
<b><math>\Gamma</math></b>				754.7	0.0
<b><math>\delta_s\text{CF}_3</math></b>	729.1	729.4	731	729.0	61
<b><math>\delta_{as}\text{CF}_3/\Delta</math></b>				574.9	19
<b><math>\gamma\text{CH}/\gamma\text{OH}</math></b>				542.4	15
<b><math>\gamma\text{OH}/\delta_{as}\text{CF}_3</math></b>				513.3	1
<b><math>\gamma\text{OH}</math></b>				494.6	79
<b><math>\delta\text{H}_3\text{C-C-OH}</math></b>				477.1	6
<b><math>\delta_{as}\text{CF}_3/\Delta</math></b>				440.6	1
<b><math>\delta\text{C=O}/\Delta</math></b>				374.7	2

$\rho\text{CF}_3$	321.1	2
$\pi\text{CF}_3/\Gamma$	258.8	1
$\Delta$	250.7	6
$\Gamma$	150.5	3
$\Delta$	139.3	0.5
$\tau\text{CH}_3$	72.0	0.2
$\tau\text{CF}_3/\tau\text{CH}_3/\Gamma$	36.4	1
$\tau\text{CH}_3/\Gamma$	22.3	1

$\nu$ , stretching;  $\delta$ , in plane bending;  $\gamma$ , out of plane bending;  $\rho$ , in plane rocking;  $\pi$ , out of plane rocking;  $\tau$ : torsion;  $\Delta$ , in plane ring deformation;  $\Gamma$ : out of plane carbon skeleton deformation;  $s$ , symmetric;  $as$ , antisymmetric. A grey background is used to identify multiplets. \* Two modes accidentally overlap in frequency and are assigned to the same experimental band

**Table S7** Vibrational assignment of the CTT(OH) isomer of trifluoroacetylacetone in neon and *para*-hydrogen. Values for argon matrices from ref. [3] are also included. Calculated harmonic frequencies [M06-2X/6-311++G(3df,3pd)] ( $\text{cm}^{-1}$ ) are added for comparison. IR intensities ( $\text{km/mol}$ ) are obtained in the harmonic approximation. Scaling factor (sf): 0.973

Assignments (simplified description)	Frequencies			Theoretical Harmonic*sf	Infrared Intensities
	Experimental				
	Ne	$\rho\text{H}_2$	Ar [3]		
$\nu\text{OH}$	3626.1	3613.5	3610	3758.1	233
$\nu\text{CH}$				3121.0	2
$\nu\text{CH}_3$	3031.5	3030.9 3022.6		3098.9	5
$\nu\text{CH}_3$	2970.9	2966.1		3042.8	3
$\nu\text{CH}_3$		2923.6		2980.6	1
$\nu\text{C}=\text{O}/\nu\text{C}=\text{C}$	1726.6	1714.7	1726	1789.8	151
$\nu\text{C}=\text{C}/\nu\text{C}=\text{O}/\delta\text{OH}$	1661.4 1659.4	1657.5	1659	1695.1	308
$\delta\text{CH}_3$	1434.5 1431.9	1433.5		1439.6	9
$\delta\text{CH}_3$	1429.5 1425.3	1428.3	1427	1431.8	16
$\delta\text{OH}/\delta\text{CH}/\nu\text{C}-\text{CF}_3/\delta\text{CH}_3$	1403.3 1402.4 1401.2	1402	1400	1405.9	265
$\delta\text{CH}_3/\nu\text{C}-\text{CH}_3$	1365.7 1362.3	1365.1 1360.7	1360	1361.7	12
$\delta\text{CH}_3/\delta\text{OH}/\nu\text{C}-\text{CF}_3/\nu\text{C}(\text{H})-\text{C}(=\text{O})$	1314.8	1314.6	1315	1319.6	50
$\nu\text{CF}_3/\delta\text{OH}$	1219.1	1217.2	1214	1249.7	268
$\delta\text{OH}/\delta\text{CH}$	1239.4	1248	1252	1249.5	160
$\nu\text{CF}_3/\delta\text{CH}$	1190.1 1188.8	1189	1189	1205.1	184
$\delta\text{CH}/\rho\text{CH}_3$	1156.5 1150.5	1157.4 1150.3	1149	1151.0	273
$\delta\text{OH}/\nu\text{CF}_3/\rho\text{CH}_3$	1117.7	1119.0	1118	1125.9	142
$\rho\text{CH}_3$	1021	1019.1	1017	1018.2	7
$\rho\text{CH}_3$	954.4	953.8	954	946.9	62
$\rho\text{CH}_3/\nu\text{C}(\text{H})-\text{C}(=\text{O})$	931.5 928.8	931.5 930.0	931	930.0	13
$\gamma\text{CH}/\Gamma$	847.6	850.6 849.1	850	863.6	12
$\nu\text{C}-\text{CF}_3/\delta_s\text{CF}_3$	779.0	778.8	779	781.3	6
$\Gamma$		676.5		685.1	2
$\Delta$		653.9	656	650.7	14
$\rho\text{CF}_3/\delta\text{F}_3\text{C}-\text{C}-\text{OH}$				583.1	41
$\pi\text{CH}_3$				574.4	5



$\delta_{asCF_3}/\Delta$	562.4	10
$\delta_{asCF_3}/\Gamma$	502.7	2
$\Delta/\delta_{asCF_3}$	433.1	1
$\nu_{OH}$	431.9	96
$\delta_{C-OH}$	380.3	6
$\Delta$	325.4	1
$\Gamma$	255.5	1
$\Delta$	236.9	7
$\Gamma$	168.5	1
$\Delta$	148.1	1
$\tau_{CH_3}$	134.4	0
$\tau_{CF_3}/\tau_{CH_3}/\Gamma$	99.4	1
$\Gamma$	18.3	3

$\nu$ , stretching;  $\delta$ , in plane bending;  $\gamma$ , out of plane bending;  $\rho$ , in plane rocking;  $\tau$ : torsion;  $\Delta$ , in plane ring deformation;  $\Gamma$ : out of plane carbon skeleton deformation;  $s$ , symmetric;  $as$ , antisymmetric. A grey background is used to identify multiplets.

**Table S8** Vibrational assignment of the TCT(OH) isomer of trifluoroacetylacetone in neon and *para*-hydrogen. Values for argon matrices from ref. [3] are also included. Calculated harmonic frequencies [M06-2X/6-311++G(3df,3pd)] (cm<sup>-1</sup>) are added for comparison. IR intensities (km/mol) are obtained in the harmonic approximation. Scaling factor (sf): 0.973

Assignments (simplified description)	Frequencies			Theoretical Harmonic*sf	Infrared Intensities
	Experimental				
	Ne	pH <sub>2</sub>	Ar [3]		
vOH	3631.8	3612.8	3604	3756.8	177
vCH	3026.1	3014.8		3155.0	5
vCH <sub>3</sub>	2983.2	2980.8		3099.6	6
vCH <sub>3</sub>	2931.8	2929.7		3057.3	2
vCH <sub>3</sub>		2902.3		2991.8	0.1
vC=O	1709.9	1709.5 1705.5	1710	1768.9	251
vC=C/ δOH	1697.2	1693.3	1693	1737.2	99
δCH <sub>3</sub>	1435.8	1434.9	1436	1440.2	10
δCH <sub>3</sub>	1424	1422.2	1421	1431.0	64
vC-O/vC-CF <sub>3</sub> /δCH <sub>3</sub>	1394.3	1394.3	1394	1405.2	96
δCH <sub>3</sub>	1369	1367.4	1366	1364.0	46
δOH/ δCH	1306.1	1306.4	1305	1303.2	42
δOH/ vC-C	1249.4	1248.3	1259	1256.4	218
δCH/ vCF <sub>3</sub>	1243.8	1242.6	1242	1242.7	183
vCF <sub>3</sub> /vC(H)-C(=O)/ δCH <sub>3</sub>	1221.2	1220.5	1217	1237.6	444
vCF <sub>3</sub>	1146 1143.5	1142.3	1142	1164.7	281
δCH/vC-O/ ρCH <sub>3</sub> /vCF <sub>3</sub>	1076.8	1077.8	1078	1084.6	12
ρCH <sub>3</sub>	1027.4	1026.4	1026	1024.9	7
ρCH <sub>3</sub> /vC-O	995.4	995.0	996	989.8	32
γCH/Γ	858.1 856.2	856.3	855	868.9	31
vC-CF <sub>3</sub> / δC=C-C	850	851.1	852	856.5	25
vC-CH <sub>3</sub> / vC(H)-C(=O)	809.9	810.9	812	809.1	7
Δ	712.7	713.4	714	709.5	18
Γ				699.5	3
δ <sub>as</sub> CF <sub>3</sub> /Δ				591.8	3
Γ				580.4	0.2
δC=O				525.5	21
δ <sub>as</sub> CF <sub>3</sub> /Γ				501.1	0.4
Δ/δ <sub>s</sub> CF <sub>3</sub>				433.4	6
Δ				363.1	2
δC-OH				307.0	14
νOH/Γ				300.3	52
Γ/γOH				278.3	30
Δ				252.0	9
τCH <sub>3</sub>				228.1	0.1
Δ				150.3	4

$\Gamma$	118.5	0.2
$\Gamma$	57.1	0.5
$\tau\text{CF}_3$	29.4	5

$\nu$ , stretching;  $\delta$ , in plane bending;  $\gamma$ , out of plane bending;  $\rho$ , in plane rocking;  $\tau$ : torsion;  $\Delta$ , in plane ring deformation;  $\Gamma$ : out of plane carbon skeleton deformation; **s**, symmetric; **as**, antisymmetric. A grey background is used to identify multiplets. **s**, symmetric; **as**, antisymmetric. A grey background is used to identify multiplets.

**Table S9** Theoretical energy (in wavelength [nm]) and intensity (oscillator strength in parentheses) for the first five singlet electronic transitions of Hexafluoroacetylacetone enol isomers computed at the TD-DFT M06-2X/6-311++G(3df,3pd) level of theory

M06-2X	
CCC	310.2 (0.001) <sup>a</sup> , <b>246.6 (0.267)<sup>b</sup></b> , 173.4 (0.001) <sup>c</sup> , 168.3 (0.008), 153.2 (0.005)
CCT	341.1 (0.000), <b>224.3 (0.348)</b> , 177.8 (0.001), 166.8 (0.000), 160.3 (0.002)
CTC	327.9 (0.000), <b>227.1 (0.334)</b> , 227.1 (0.334), 191.4 (0.002), 172.3 (0.000)
CTT	328.1 (0.000) <sup>a</sup> , <b>230.0 (0.346)<sup>b</sup></b> , 178.6 (0.001) <sup>c</sup> , 168.2 (0.000), 163.0 (0.011)
TCC	323.7 (0.000) <sup>a</sup> , <b>226.5 (0.366)<sup>b</sup></b> , 169.0 (0.010) <sup>c</sup> , 164.6 (0.003), 157.4 (0.002)
TCT	330.6 (0.000), <b>220.2 (0.398)</b> , 176.6 (0.002), 163.9 (0.002), 158.9 (0.001)
TTC	320.4 (0.003), <b>227.3 (0.199)</b> , 190.5 (0.022), 171.2 (0.027), 166.8 (0.096)
TTT	323.0 (0.002), <b>227.6 (0.238)</b> , 177.1 (0.001), 170.2 (0.095), 167.2 (0.030)

The electronic transitions are classified for the experimentally observed isomers, even when there is a slight loss of planarity in the carbon skeleton for some isomers: <sup>a</sup>  $n \rightarrow \pi^*$  transition, <sup>b</sup>  $\pi \rightarrow \pi^*$  transition, <sup>c</sup>  $\pi \rightarrow \sigma^*$  transition

**Table S10** Theoretical energy (in wavelength [nm]) and intensity (oscillator strength in parentheses) for the first five singlet electronic transitions of Trifluoroacetylacetone enol isomers computed at the TD-DFT M06-2X/6-311++G(3df, 3pd) level of theory

M06-2X	
CO	
CCC	294.9 (0.001) <sup>a</sup> , <b>245.1 (0.301)<sup>b</sup></b> , 189.5 (0.005) <sup>c</sup> , 168.9 (0.000), 168.0 (0.006)
CCT	327.6 (0.000), <b>229.1 (0.384)</b> , 203.9 (0.000), 178.5 (0.013), 174.6 (0.014)
CTC	312.4 (0.000) <sup>a</sup> , <b>232.9 (0.355)<sup>b</sup></b> , 202.3 (0.001) <sup>c</sup> , 172.5 (0.000), 166.9 (0.025)
CTT	313.5 (0.000), <b>235.1 (0.362)</b> , 199.9 (0.000), 175.1 (0.011), 168.3 (0.004)
TCC	312.1 (0.001), <b>233.1 (0.404)</b> , 190.2 (0.006), 169.2 (0.003), 165.6 (0.015)
TCT	317.6 (0.000), <b>226.1 (0.435)</b> , 203.5 (0.000), 178.2 (0.012), 169.0 (0.010)
TTC	309.6 (0.000), <b>227.6 (0.428)</b> , 202.4 (0.003), 173.0 (0.001), 168.3 (0.013)
TTT	312.4 (0.001), <b>228.9 (0.446)</b> , 200.9 (0.001), 175.2 (0.014), 169.9 (0.006)
OH	
CCC	303.2 (0.001) <sup>a</sup> , <b>239.4 (0.270)<sup>b</sup></b> , 192.1 (0.006) <sup>c</sup> , 186.3 (0.025), 178.2 (0.000)
CCT	339.7 (0.000), <b>214.1 (0.370)</b> , 186.3 (0.003), 183.1 (0.007), 173.8 (0.001)
CTC	326.0 (0.000), <b>218.3 (0.331)</b> , 202.7 (0.002), 183.9 (0.014), 173.8 (0.001)
CTT	326.2 (0.000) <sup>a</sup> , <b>220.8 (0.347)<sup>b</sup></b> , 187.5 (0.002) <sup>c</sup> , 177.6 (0.013), 176.8 (0.008)
TCC	320.7 (0.000), <b>212.1 (0.378)</b> , 184.4 (0.003), 174.8 (0.032), 164.9 (0.000)
TCT	328.0 (0.000) <sup>a</sup> , <b>206.8 (0.418)<sup>b</sup></b> , 186.4 (0.002) <sup>c</sup> , 176.7 (0.025), 169.8 (0.000)
TTC	325.1 (0.001), <b>214.4 (0.376)</b> , 196.9 (0.003), 176.6 (0.022), 169.8 (0.004)
TTT	325.6 (0.001), <b>214.8 (0.405)</b> , 188.2 (0.001), 173.2 (0.017), 170.1 (0.021)

The electronic transitions are classified for the experimentally observed isomers, even when there is a slight loss of planarity in the carbon skeleton for some isomers: <sup>a</sup>  $n \rightarrow \pi^*$  transition, <sup>b</sup>  $\pi \rightarrow \pi^*$  transition, <sup>c</sup>  $\pi \rightarrow \sigma^*$  transition

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