

Electronic Supplementary Information

(ESI)

Which strategy for molecular probe design?

An answer from the integration of spectroscopy and QM modeling

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TABLES

Tables S1: Computed energies (Hartree), relative energies (kcal/mol) and relative populations (%) at 300 K for **AcAn1** and **AcAn2** in vacuo and in each solvent.

	E (Hartree)		E (kcal/mol)		Population at 300 K (%)	
	AcAn1	AcAn2	AcAn1	AcAn2	AcAn1	AcAn2
Vacuo	-692.140755	-692.141805	3.409	4.009	21.9	78.1
Hexane	-692.146475	-692.147442	3.955	4.693	23.6	76.4
Acetone	-692.157548	-692.158647	4.971	5.075	20.9	79.1
DMSO	-692.158488	-692.159559	5.055	6.093	21.4	78.6
EtOH	-692.157825	-692.158931	4.988	6.016	20.7	79.3
MeOH	-692.158300	-692.159403	5.024	6.062	20.8	79.2
Water	-692.151396	-692.152469	4.866	5.905	21.4	78.6

Tables S2.n: DFT calculated and experimentally determined infrared frequencies (cm^{-1}) and intensities of **AcAn** in different solvents. The intensities are normalized with respect to the sum of all the intensities and multiplied by 100.

1. Hexane					
AcAn1		AcAn2		Exp	
Scl. Freq. (cm-1)	Norm. Int.	Scl. Freq. (cm-1)	Norm. Int.	Freq. (cm-1)	Norm. Int.
613.3	0.9	613.9	0.8	621.5	1.3
626.0	0.7	631.2	0.7	639.9	0.9
860.9	2.6	851.2	1.0	822.0	1.3
937.3	0.3	936.4	0.3	942.3	0.9
962.5	0.7	995.0	0.5	964.2	1.3
1148.3	1.9	1046.9	0.9	1150.6	0.9
1173.9	5.5	1176.6	1.7	1184.7	8.9
1208.4	19.2	1212.0	14.9	1217.5	20.1
1331.5	0.7	1331.0	1.6	1312.2	6.7
---	---	1614.9	0.4	1647.5	3.6
---	---	---	---	1676.6	1.3
1675.1	17.0	1667.1	29.4	1687.6	33.5
2992.2	0.5	2996.3	0.5	2934.9	3.1
3071.9	1.4	3051.8	0.7	3071.5	6.7
3089.6	0.7	3061.6	1.6	3092.3	9.4
R(B/A)	0.9		2.0		1.7

2. CCl ₄					
AcAn1		AcAn2		Exp	
Scl. Freq. (cm-1)	Norm. Int.	Scl. Freq. (cm-1)	Norm. Int.	Freq. (cm-1)	Norm. Int.
634.8	0.8	634.9	0.4	634.0	0.8
1148.9	1.9	1137.9	2.2	1151.4	0.6
1174.0	5.7	1176.9	1.8	1168.7	0.6
1208.2	19.1	1211.6	15.1	1218.9	17.0
1252.5	1.3	1253.8	1.7	1228.9	17.0
1331.6	0.7	1331.1	15.6	1312.1	1.6
---	---	1346.2	1.5	1343.1	1.6
1356.7	0.9	1355.8	2.5	1353.2	2.9
1386.4	3.5	1390.9	1.8	1364.2	1.6
1420.0	0.5	1421.0	0.9	1414.4	1.6
1434.8	1.2	1435.5	0.9	1432.6	1.6
1446.1	1.0	1445.2	0.8	1458.2	0.7
1470.5	0.5	1466.3	1.6	1478.9	1.3
---	---	1608.4	6.9	1612.4	5.2
1673.3	16.7	1665.9	29.4	1683.5	31.3
2990.2	0.4	2994.9	0.4	3012.3	1.6
3080.0	1.8	3068.9	1.8	3056.3	6.7
R(B/A)	0.9		1.9		1.8

3. CHCl ₃					
AcAn1		AcAn2		Exp	
Sclد. Freq. (cm-1)	Norm. Int.	Sclد. Freq. (cm-1)	Norm. Int.	Freq. (cm-1)	Norm. Int.
613.0	0.9	613.5	0.8	608.0	0.6
626.3	0.7	631.4	0.6	626.0	0.7
634.4	0.8	634.4	0.4	635.0	0.2
862.7	2.2	854.6	0.9	865.0	0.9
879.2	1.1	880.8	2.4	878.0	2.4
---	---	896.2	1.8	891.0	1.9
917.9	1.6	924.2	2.9	927.0	2.2
940.6	0.3	940.1	0.3	948.0	0.6
993.5	0.4	994.3	0.5	1012.0	0.7
1049.9	0.3	1046.8	1.2	1053.0	1.1
1147.7	1.9	1136.1	1.9	1152.0	1.9
1207.5	18.6	1211.7	14.8	---	---
1252.2	0.4	1253.3	0.7	1251.0	1.8
---	---	1291.5	5.1	1293.0	4.4
1330.7	0.8	1330.3	1.8	1331.0	1.7
1355.4	4.0	1345.5	0.8	1364.0	0.7
1385.6	3.8	1354.8	2.3	1391.0	2.4
1418.9	0.5	1420.0	1.0	1402.0	1.3
1431.5	1.2	1432.1	1.0	1415.0	1.3
1438.4	0.8	1439.0	0.7	1434.0	1.0
1444.8	1.1	1444.1	0.9	1444.0	0.8
1469.3	0.6	1465.2	1.9	1463.0	2.3
1566.5	3.4	1570.6	0.4	1579.0	4.9
---	---	1606.1	9.2	1602.0	13.7
---	---	1613.5	0.4	1627.0	3.1
1663.5	16.4	1652.9	29.7	1673.0	28.1
2988.5	0.3	2992.8	0.3	2997.0	6.4
3063.7	1.3	3064.1	1.2	3065.0	4.0
3074.5	1.0	3074.8	1.0	3073.0	3.9
R(B/A)	0.9		2.0		---

4. EtOH					
AcAn1		AcAn2		Exp	
Sclد. Freq. (cm-1)	Norm. Int.	Sclد. Freq. (cm-1)	Norm. Int.	Freq. (cm-1)	Norm. Int.
943.2	0.3	943.0	0.3	942.3	2.6
1207.3	17.9	1211.9	14.1	---	---
---	---	1603.4	13.3	1616.1	3.8
---	---	1612.0	0.3	---	---
1651.5	15.7	1639.4	27.7	1667.8	28.2
R(B/A)	0.9		2.0		---

5. MeOH					
AcAn1		AcAn2		Exp	
Sclد. Freq. (cm-1)	Norm. Int.	Sclد. Freq. (cm-1)	Norm. Int.	Freq. (cm-1)	Norm. Int.
863.8	1.9	857.9	0.9	862.0	1.1
992.0	1.3	992.9	0.6	964.0	0.5
1207.6	17.7	1212.3	13.9	1202.0	23.1
1564.6	4.4	1568.9	0.5	1565.0	0.5
---	---	1603.1	13.9	1617.5	25.6
1651.4	15.4	1637.5	27.1	1662.2	49.7
R(B/A)	0.9		2.0		2.1
R(B*/B)	---		1.0		1.1

6. CH ₃ CN					
AcAn1		AcAn2		Exp	
Sclد. Freq. (cm-1)	Norm. Int.	Sclد. Freq. (cm-1)	Norm. Int.	Freq. (cm-1)	Norm. Int.
634.0	0.7	634.3	0.4	642.9	1.6
788.1	0.4	798.6	0.4	807.9	0.5
880.4	1.2	881.7	2.1	875.4	1.1
962.8	2.2	943.2	0.3	965.9	1.6
---	---	1134.3	1.5	1152.9	6.4
1172.3	5.4	1175.7	1.8	1178.9	7.5
1207.2	16.8	1211.9	14.0	1231.9	23.0
1288.6	1.0	1290.9	5.2	1280.3	8.6
1652.2	14.6	1638.2	27.3	1657.2	49.7
R(B/A)	0.9		1.9		2.2

7. DMSO					
AcAn1		AcAn2		Exp	
Scld. Freq. (cm-1)	Norm. Int.	Scld. Freq. (cm-1)	Norm. Int.	Freq. (cm-1)	Norm. Int.
581.6	0.5	592.8	0.5	598.0	0.6
728.7	3.2	729.6	2.6	734.0	0.6
864.0	1.9	858.1	0.8	827.0	0.6
1207.3	17.7	1212.0	14.0	1224.0	31.3
1384.6	4.2	1353.7	2.0	1364.0	0.6
1519.9	3.9	1568.8	0.5	1560.0	0.6
1651.9	15.4	1637.8	27.2	1654.0	65.8
R(B/A)	0.9		1.9		2.1

Table S3.1: ^1H NMR chemical shifts of **AcAn**, experimentally determined and theoretically predicted, via the IEF-PCM methods at GIAO-DFT level, in various solvents. The labelling refers to Figure 1 of the paper; moreover the label “CH₃” indicate the methyl unit, where an average of chemical shift values for H27, H28 and H29 was calculated. The average of absolute residuals (AAR) is also reported in order to compare the experimental with the theoretical data.

		CCl₄	CDCl₃	EtOD	MeOD	CD₃CN	DMSO
EXP	H12	8.4	8.5	8.7	8.8	8.7	8.6
	H16	8.9	8.8	8.9	9	8.7	8.8
	H17	7.7	7.9	7.8	7.7	7.8	7.9
	H18	8.4	8.5	8.7	8.8	8.7	8.6
	H19	8.4	8.5	8.7	8.8	8.7	8.6
	H20	7.7	7.9	7.8	7.7	8.2	8.1
	H21	9.2	8.9	9.2	9.2	9.1	8.9
	H22	8.2	8.2	8.3	8.2	8.2	8.2
	H23	9.4	9.2	9.2	9.2	9.1	9.4
	CH ₃	2.4	2.4	2.8	2.9	2.8	2.7
AcAn1	H12	8.4	8.5	8.6	8.6	8.6	8.7
	H16	8.7	8.9	9.0	9.0	9.0	9.0
	H17	7.8	7.9	8.0	8.0	8.0	8.0
	H18	8.4	8.5	8.6	8.6	8.6	8.6
	H19	8.4	8.5	8.6	8.6	8.6	8.6
	H20	7.8	7.9	8.0	8.0	8.0	8.0
	H21	9.0	9.1	9.2	9.2	9.2	9.2
	H22	8.1	8.2	8.4	8.4	8.4	8.4
	H23	9.4	9.4	9.4	9.4	9.4	9.4
	CH ₃	2.7	2.8	2.8	2.8	2.8	2.8
	AAR	0.11	0.10	0.12	0.18	0.17	0.12
AcAn2	H12	8.4	8.5	8.6	8.6	8.6	8.6
	H16	8.7	8.8	9.0	9.0	9.0	9.0
	H17	7.8	7.9	8.0	8.0	8.0	8.1
	H18	8.4	8.5	8.6	8.6	8.6	8.6
	H19	8.4	8.5	8.6	8.6	8.6	8.6
	H20	7.8	7.9	8.0	8.0	8.0	8.1
	H21	9.0	9.0	9.2	9.2	9.2	9.2
	H22	8.5	8.5	8.4	8.4	8.4	8.4
	H23	9.1	9.1	9.2	9.2	9.2	9.2
	CH ₃	2.7	2.8	2.8	2.8	2.9	2.8
	AAR	0.15	0.11	0.11	0.17	0.15	0.13

Table S3.2: Experimental ^{13}C NMR chemical shifts of **AcAn** determined in various solvents. The labelling refers to Figure 1 of the paper.

	CCl₄	CDCl₃	EtOD	MeOD	CD₃CN	DMSO
C1	126.2	126.2	127.4	127	127.1	127.5
C2	126.7	126.6	127.4	127.3	127.1	127.5
C3	132.3	132.1	132.7	132.4	132.3	132.8
C4	131.2	131.6	129.7	131.1	129.8	130.8
C5	128.4	128.4	128.6	128.7	128.5	128.6
C6	125.7	125.9	125.7	126	125.2	125.3
C7	124.5	124.8	125.7	126	125.2	125.3
C8	129.1	129.3	129.7	130.7	129.8	129.7
C9	128.7	128.7	128.6	128.7	128.5	128.3
C10	131.2	131.6	130.7	130.7	130.9	130.8
C11	126.7	126.6	127.4	128.4	127.2	127.5
C13	123.3	122.7	121.4	122.6	121.3	121.5
C14	130.8	130.3	130.2	130.7	130.4	130.8
C15	130.8	131.2	134.3	133.3	133.6	132.8
C24	198.9	200.3	201.5	201.2	201.3	201.7
C26	25.6	25.5	24.7	24.5	24.3	23.9

Table S3.3: GIAO-DFT ^{13}C NMR chemical shifts of **AcAn1** conformer calculated via the IEF-PCM methods in various solvents. The average of absolute residuals (AAR) is also reported in order to compare the experimental with the theoretical data. The labelling refers to Figure 1 of the paper.

	CCl₄	CDCl₃	EtOD	MeOD	CD₃CN	DMSO
C1	126.1	126.6	127.2	127.2	127.0	127.2
C2	126.8	126.9	127.2	127.2	127.1	127.3
C3	132.2	132.3	132.5	132.5	132.4	132.5
C4	130.9	131.0	131.0	131.0	131.0	131.0
C5	128.2	128.3	128.6	128.6	128.4	128.6
C6	124.8	125.2	125.7	125.7	125.6	125.8
C7	124.4	124.7	125.1	125.1	125.0	125.2
C8	130.4	130.6	131.0	131.0	130.8	131.0
C9	128.5	128.4	128.3	128.3	128.2	128.3
C10	131.3	131.4	131.5	131.5	131.4	131.5
C11	126.7	127.1	127.7	127.8	127.5	127.8
C13	123.6	123.9	124.3	124.4	124.2	124.4
C14	130.3	130.2	130.0	130.0	130.1	129.9
C15	130.9	130.9	131.0	130.9	130.7	130.9
C24	197.9	200.0	202.1	202.3	202.2	202.4
C26	22.2	22.5	22.9	22.9	22.8	22.9
AAR	0.7	0.8	0.9	0.8	0.8	1.3

Table S3.4: GIAO-DFT ^{13}C NMR chemical shifts of **AcAn2** conformer calculated via the IEF-PCM methods in various solvents. The average of absolute residuals (AAR) is also reported in order to compare the experimental with the theoretical data. The labelling refers to Figure 1 of the paper.

	CCl₄	CDCl₃	EtOD	MeOD	CD₃CN	DMSO
C1	126.0	126.5	127.1	127.2	127.0	127.2
C2	126.9	127.0	127.3	127.3	127.1	127.3
C3	132.3	132.5	132.7	132.7	132.6	132.7
C4	130.9	131.0	131.1	131.1	131.0	131.1
C5	127.9	128.2	128.6	128.7	128.5	128.7
C6	124.9	125.3	125.8	125.8	125.7	125.8
C7	124.7	124.9	125.2	125.2	125.1	125.2
C8	128.7	129.2	130.1	130.1	129.9	130.2
C9	128.7	128.6	128.6	128.7	128.5	128.6
C10	131.5	131.5	131.5	131.5	131.4	131.5
C11	127.3	127.5	128.0	128.0	127.8	128.0
C13	122.1	121.6	121.2	121.2	121.1	121.2
C14	131.5	131.1	130.6	130.6	130.7	130.6
C15	132.8	133.5	134.8	134.9	134.7	134.9
C24	199.9	200.1	202.1	202.3	202.2	202.4
C26	20.8	21.1	21.4	21.5	21.4	21.4
AAR	0.9	0.9	0.8	0.8	0.8	1.1

Table S4 CAM-B3LYP vibrational frequencies (with respect to 0-0 transition) and FC intensities of modes which most contribute to the vibronic structure of the excitation I band of **AcAn2**.

Norm.Mod	Hexane		DMSO		MeOH		MeOH(+1MeOH)	
	ν [cm ⁻¹]	Int.[a.u.]	ν [cm ⁻¹]	Int.[a.u.]	ν [cm ⁻¹]	Int.[a.u.]	ν [cm ⁻¹]	Int.[a.u.]
1	130	0.04	135	0.04	134	0.03	184	0.01
2	300	0.10	302	0.10	302	0.10	302	0.02
3	383	0.03	385	0.02	384	0.02	384	0.02
4	430	0.05	430	0.05	430	0.06	435	0.02
5	1185	0.02	1178	0.02	1177	0.02	1179	0.01
6	1267	0.02	1265	0.02	1264	0.02	1264	0.01
7	1378	0.08	1373	0.10	1373	0.10	1369	0.03
8	1424	0.2	1415	0.09	1415	0.09	1418	0.02
9	1518	0.02	1511	0.06	1511	0.06	1523	0.01
10	1570	0.10	1569	0.09	1569	0.09	1573	0.02
11	1618	0.02	1569	0.09	1568	0.09	1564	0.01
12	1718	0.02	1674	0.02	1673	0.02	1632	0.01
13	604*	0.02	604*	0.02	604*	0.02	604*	0.03
14	2830*	0.01	2831*	0.01	2830*	0.01	2826*	0.01

Assignment of Normal Modes:

1. ρ CH₃ + ρ CH(ring A)
2. ρ C=O + ρ CH(ring C)
3. δ_s CH₃ + ρ C=C(ring B) + ρ CH(ring A)
4. δ_s CH₃ + ν_s C=C(ring B) + ρ CH(ring C)
5. δ_s CH(ring A)
6. δ_s CH(rings A,B,C) + ν_s C_{Ar}-CO
7. ρ CH (ring A) + ν_{as} C=C (rings B,C)
8. ρ CH (ring B) + ν_{as} C=C (rings A,B)
9. δ_s CH(rings A,C) + ν_s C=C (rings A,B)
10. ρ CH (ring C) + ν_{as} C=C (rings A,C)
11. δ_s CH(rings A,B,C) + ν_{as} C=C (rings A,B,C)
12. ν_s C=O + ρ_s CH(ring C)

Nomenclature: ν_{as} asymmetrical stretching, ν_s symmetrical stretching, δ_s in-plane bending (scissoring), ρ in-plane bending (rocking), ω out-of-plane bending (wagging), τ out-of-plane bending (twisting).

FIGURES

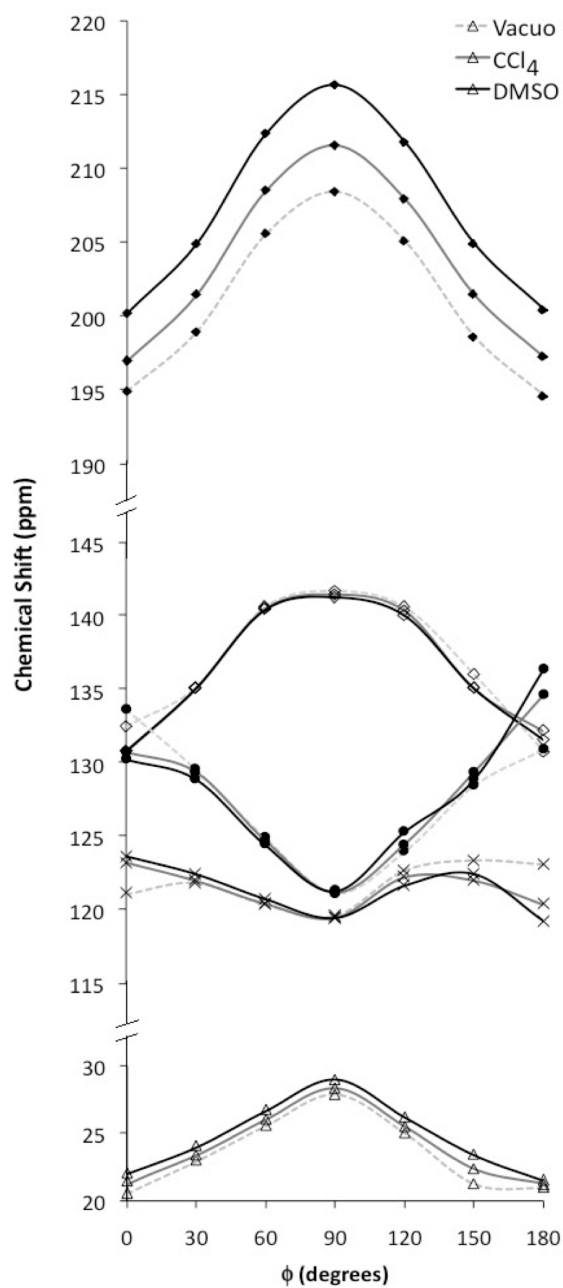


Figure S2: Plot of the isotropic chemical shifts for carbons C26 (open triangles), C13 (crosses), C14 (open rhombs), C15 (filled circles) and C24 (filled rhombs) of **AcAn** in function of variation of dihedral angle ϕ .

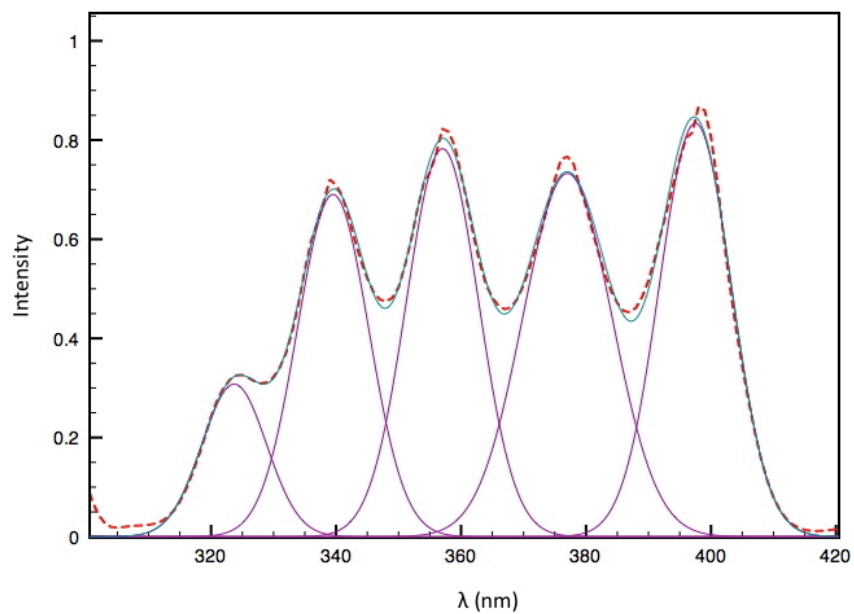


Figure S3: Deconvolution of the vibronic band in the absorption spectrum of **AcAn** dissolved in Heptane.

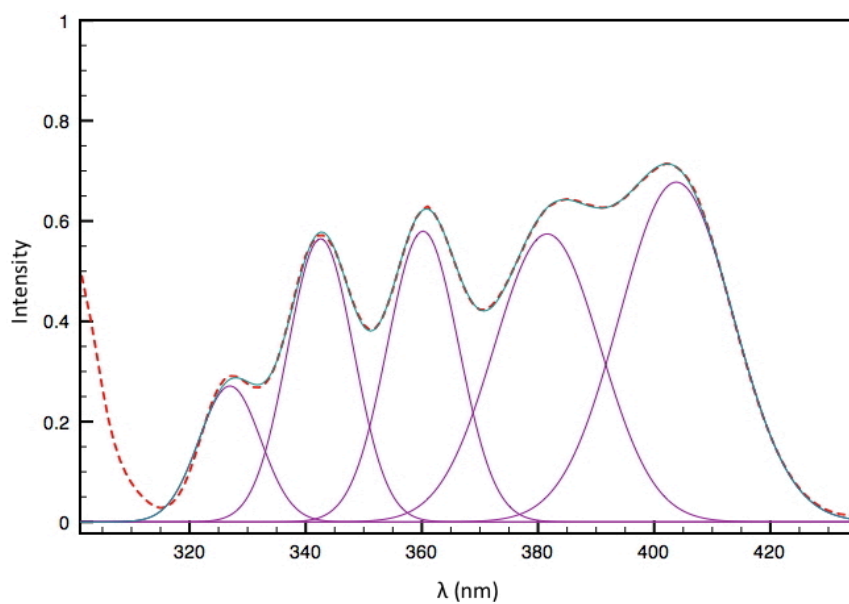


Figure S4: Deconvolution of the vibronic band in the absorption spectrum of **AcAn** dissolved in DMSO.

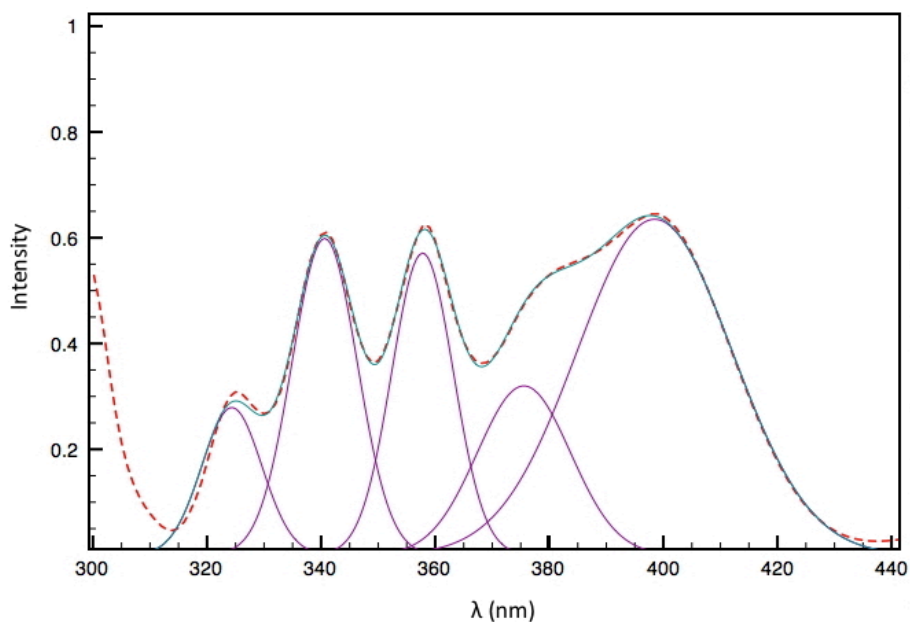


Figure S5: Deconvolution of the vibronic band in the absorption spectrum of **AcAn** dissolved in Methanol. Here the two low frequency peaks are fitted with two broad gaussians.

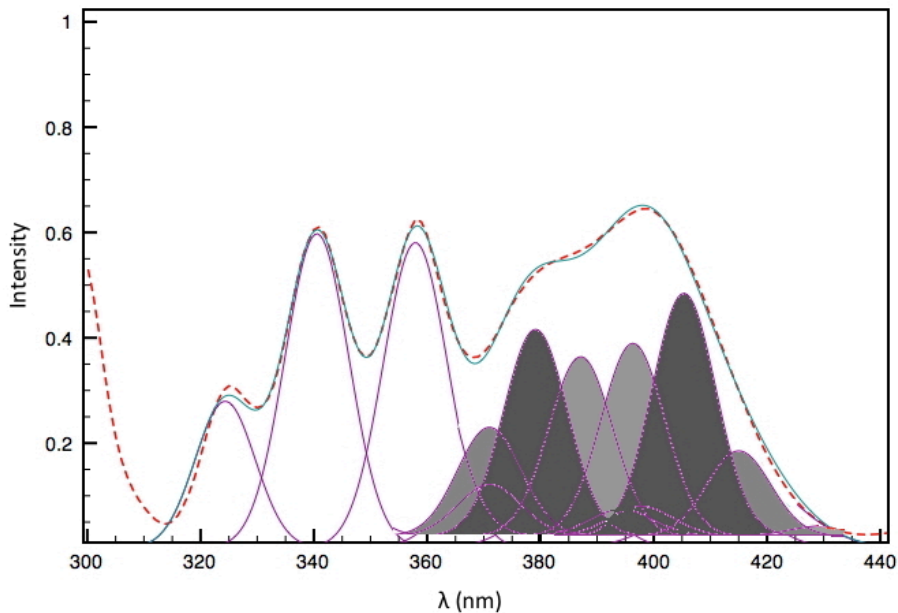


Figure S6: Deconvolution of the vibronic band in the absorption spectrum of **AcAn** dissolved in Methanol. Here the two low frequency peaks are fitted with five gaussians each, with a line broadening comparable to the ones used in the fitting of the higher frequency peaks.