SM1 : Calculated and experimental vibrational properties of water and diacetyl monomer. Harmonic frequencies, [anharmonic frequencies], (harmonic IR intensities), *experimental frequencies.* Wavenumbers in cm^{-1}, intensities in $km.mol^{-1}$

		Ab initio			Experiment		
	Vibrational mode (symmetry)	MP2/AVTZ			IR Gaz[a]	IR Ne Matrix[b]	Raman Liquid[c]
H_2O	ν_{OH} as (b2)	3948	[3768]	(75)	3756	3759	
	ν_{OH} s (a1)	3822	[3654]	(6)	3657	3665	
	δ (a1)	1628	[1578]	(72)	1595	1596	
Diacetyl	νCH_3 as (b_u)	3209	[3065]	(7)	3024	3037	
	νCH_3 as (a_g)	3209	[3065]	(0)			3016
	νCH_3 as (b_g)	3164	[3019]	(0)			2978
	νCH_3 as (a_u)	3163	[3019]	(2)	2979	2995	
	νCH_3 s (b_u)	3083	[2969]	(1)	2945	2947	
	νCH_3 s (a_g)	3083	[2969]	(0)			2928
	$\nu C{=}O$ as (b_u)	1736	[1703]	(166)	1729	1731	
	$\nu C{=}O$ s (a_g)	1734	[1696]	(0)			1720
	δCH_3 as (b_g)	1485	[1431]	(0)			1431
	δCH_3 as (a_u)	1480	[1428]	(20)	1426	1433	
	δCH_3 as (b_u)	1473	[1429]	(31)	1424	1426	
	δCH_3 as (a_g)	1473	[1427]	(0)			1424
	δCH_3 s (a_g)	1408	[1365]	(0)			1364
	δCH_3 s (b_u)	1395	[1353]	(58)	1360	1358	
	νC-C (ag)	1309	[1277]	(0)			1275
	γCH_3 (b_u)	1147	[1120]	(67)	1116	1121	
	γCH_3 (b_g)	1073	[1046]	(0)			1050
	γCH_3 (a_g)	1018	[998]	(0)			1005
	γCH_3 (a_u)	968	[943]	(4)	950	950	
	νC-CH_3 as (b_u)	927	[908]	(20)	912	907	
	νC-CH_3 s (a_g)	704	[686]	(0)			685
	γC =O s (b_g)	619	[609]	(0)			608
	$\delta C{=}O$ as (b_u)	539	[535]	(39)	540	540	
	$\delta C{=}O$ s (a_g)	526	[521]	(0)			537
	δC-C-C s (a_g)	363	[363]	(0)			369
	γC =O as (a_u)	345	[348]	(6)	340	348	
	δC-C-C as (b_u)	239	[253]	(16)	249	251	
	τCH_3 s (b_g)	128	[121]	(0)			
	τCH_3 as (a_u)	127	[121]	(0)	112		
	τC-C (a_u)	55	[47]	(11)	48		

ν : stretching δ : bending γ : rocking τ : torsion s: symmetric as: antisymmetric
Experimental data from Refs 23 and 24 (a), this work (b) and Ref 25 (c).

SM2 : Calculated vibrational properties of the three isomers of 1/1 complex at MP2/AVTZ level of theory. Harmonic frequencies, [anharmonic frequencies], (harmonic IR intensities). Wavenumbers in cm^{-1}, intensities in $km.mol^{-1}$

		S1			S2			S3		
H_2O	ν_{OH} as (b2)	3911	[3733]	(135)	3911	[3737]	(152	3924	[3742]	(90)
	ν_{OH} s (a1)	3701	[3548]	(334)	3731	[3582]	(298)	3792	[3624]	(10)
	δ (a1)	1645	[1594]	(90)	1646	[1593]	(62)	1620	[1577]	(133)
Diacetyl	νCH_3 as (b_u)	3211	[3071]	(2)	3211	[3075]	(4)	3208	[3063]	(7)
	νCH_3 as (a_g)	3209	[3066]	(4)	3209	[3071]	(3)	3207	[3064]	(0)
	νCH_3 as (b_g)	3163	[3021]	(1)	3164	[3026]	(0)	3168	[3027]	(0)
	νCH_3 as (a_u)	3160	[3018]	(0)	3160	[3021]	(0)	3166	[3022]	(1)
	νCH_3 s (b_u)	3083	[2970]	(0)	3084	[2972]	(0)	3083	[2970]	(1)
	νCH_3 s (a_g)	3081	[2970]	(1)	3083	[2969]	(2)	3083	[2973]	(2)
	νC=O as (b_u)	1736	[1703]	(98)	1735	[1702]	(161)	1737	[1706]	(151)
	νC=O s (a_g)	1730	[1692]	(67)	1732	[1697]	(40)	1735	[1699]	(6)
	δCH_3 as (b_g)	1486	[1432]	(0)	1487	[1434]	(4)	1489	[1431]	(9)
	δCH_3 as (a_u)	1481	[1430]	(19)	1480	[1430]	(17)	1482	[1431]	(6)
	δCH_3 as (b_u)	1475	[1430]	(19)	1472	[1432]	(44)	1477	[1434]	(19)
	δCH_3 as (a_g)	1474	[1432]	(6)	1470	[1431]	(4)	1472	[1428]	(15)
	δCH_3 s (a_g)	1412	[1372]	(5)	1410	[1373]	(0)	1406	[1365]	(1)
	δCH_3 s (b_u)	1398	[1358]	(58)	1396	[1361]	(60)	1391	[1350]	(63)
	νC-C (ag)	1315	[1280]	(0)	1311	[1281]	(0)	1310	[1279]	(0)
	γCH_3 (b_u)	1154	[1126]	(70)	1152	[1125]	(60)	1150	[1121]	(63)
	γCH_3 (b_g)	1075	[1047]	(0)	1071	[1047]	(0)	1074	[1046]	(0)
	γCH_3 (a_g)	1023	[1002]	(0)	1023	[1002]	(0)	1021	[999]	(0)
	γCH_3 (a_u)	971	[945]	(5)	965	[946]	(4)	970	[947]	(8)
	$\nu C\text{-}CH_3$ as (b_u)	931	[911]	(18)	933	[914]	(16)	930	[911]	(18)
	$\nu C\text{-}CH_3$ s (a_g)	709	[707]	(0)	706	[693]	(0)	706	[690]	(0)
	γC =O s (b_g)	620	[610]	(0)	619	[615]	(1)	617	[610]	(0)
	δC=O as (b_u)	548	[545]	(37)	546	[542]	(39)	541	[537]	(42)
	δC=O s (a_g)	532	[527]	(1)	526	[522]	(1)	529	[523]	(0)
	δC-C-C s (a_g)	372	[364]	(8)	369	[390]	(0)	370	[368]	(1)
	γC =O as (a_u)	348	[348]	(2)	347	[352]	(5)	348	[333]	(6)
	δC-C-C as (b_u)	255	[247]	(50)	244	[236]	(15)	246	[231]	(35)
	τCH_3 s (b_g)	130	[138]	(0)	176	[188]	(14)	145	[117]	(1)
	τCH_3 as (a_u)	123	[87]	(10)	129	[138]	(0)	122	[122]	(2)
	τC-C (a_u)	51	[45]	(1)	57	[68]	(3)	45	[51]	(6)
Intermolecular	δH_2O	542	[479]	(60)	525	[407]	(60)	309	[231]	(46)
	γH_2Ob	370	[315]	(129)	326	[297]	(143)	238	[208]	(72)
	vinter	138	[119]	(0)	143	[130]	(3)	139	[122]	(29)
	γH_2Of	102	[14]	(118)	153	[140]	(110)	159	[138]	(113)
	δDAC	81	[54]	(7)	87	[74]	(5)	85	[88]	(18)
	γDAC	30	[25]	(3)	8	[108]	(1)	26	[1]	(4)

ν: stretching δ : bending γ : rocking τ : torsion s: symmetric as: antisymmetric

For clarity, the nomenclature used for the water and DAC vibration modes in the complexes is that of the isolated monomers, although obviously their symmetry no longer exists in the complexes.