SUPPORTING MATERIAL ACCOMPANYING THE ARTICLE:

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Luminescence and Raman spectra of acetylacetone at low temperatures,

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Additional Table 1. Observed Raman and infrared bands of acetylacetone (cm^{-1}). The assignment of matrix bands is based on B1LYP/6-311G(d,p) calculation for SYN and TS2 enols from ref. [7]. Bands printed in bald type are very broad luminescent bands that underlie the vibrational spectra. Assignment of keto bands is based on B3LYP/6-31++G(d.p) calculation[40], this work.

Raman matrix 10 K	Raman solid 10 K enols+keto	Raman solid 10 K enols+keto	Raman solid 10 K enols	Raman liquid 295 K enols+keto	Infrared liquid 295 K enols+keto	Assignment
	4906 m,vbr	**4900 vs,vbr**	**5354 vs,vbr**			Luminescent band
3496 vw						impurity, H_3OH?
3113 w	3109 mw	3114 w	3113 mw			Combination of C=C-C=O str. and $\delta_a(CH_3)$ SYN enol
				3095 w,br	3093 mw,sh	CH stretching SYN enol in liquid
3082 w	3089 mw	3086 w	3081 w	3075 w,sh		CH stretching SYN enol in matrix and crystal
3014 mw		3016 m	3017 m		3008 mw	CH_3 asym stretch. SYN enol
	3009 mw	3004 mw,sh	3009 m	3003 m		CH_3 asym.stretch. SYN enol
2979 m	2981 mw,sh	2980 w,sh				CH_3 asym. stretch. S
			2973 mw,sh			CH_3 asym. stretch crystal splitting
	2969	2968 m	2969 s	2965 m,sh	2968 mw	CH_3 asym. stretch. S
2934 vs	2925 vs	2924 vs	2925 vs	2925 vs	2928 mw	CH_3 sym.stretch. SYN enol
2855 w,br	2841 w	2847 vw	2849 w,br	2846 w	2844 w	Combination

Additional Table 1. continued

Raman matrix 10 K enols	Raman solid 10 K enols+keto	Raman solid 10 K enols+ keto	Raman solid 10 K enols	Raman liquid 295 K enols+keto	Infrared liquid 295 K enols + keto	Assignment
					2796 w	Combination
2721 w		2719 vw		2714 w	2707 w	Combination
					2636 w	Combination
2328 s						N_2 stretch
					1994 w	Combination
					1922 w	Combination
	1800 m,vbr					Luminescent band
	1715 w	1715 vvw		1732 w	1730 s	ν(C=O) keto, out of phase
	1700 w	1698 vvw			1709 s	ν (C=O) keto, in phase
1687 w,sh			1683 w			ν(C=C-C=O) TS2 enol
				1672 br,sh		
	1651 mw.sh	1653 mw,sh	1652 mw,sh			ν(C=C-C=O) SYN enol, crystal spliting
1629 m,sh	1634 m	1638 mw	1634 ms		1622 vs,vbr	ν (C=C-C=O) SYN enol
1617 m,sh						ν(C=O)+ δ(O-H) TS2 enol
1602 s	1605 m	1605 m	1607 ms	1604 s,br		ν(C=O) + δ(O-H) SYN enol
	1585 mw,sh	1583 mw	1585 m			ν (C=O) + δ(O-H) SYN enol, crystal splitting
1554 m						O_2

Table 1. continued

Raman matrix 10 K enols	Raman solid 10 K enols+keto	Raman solid 10 K enols+ keto	Raman solid 10 K enols	Raman liquid 295 K enols+keto	Infrared liquid 295 K enols + keto	Assignment
1470 w, br				1490 w,sh		$\delta a(CH_3)$ asym. bend. TS2 enol
1464 mw	1455 m	1454 m	1455 m		1462 m,sh	$\delta a(CH_3)$ asym. bend. SYN enol
	1445 mw,sh	1441 mw	1442 mw			$\delta a(CH_3)$ asym.bend SYN enol crystal splitting
1434 m				1433 mw,br		$\delta a(CH_3)$ asym. bend. SYN enol
1423 mw,sh	1425 mw	1427 m	1426 m		1424 s,br	$\delta a(CH_3)$ asym. bend. SYN enol
	1406 w	1408 w,sh	1409 w			
1375 m	1378 ms	1377 m	1378 s	1372 ms	1363 s	$\delta s(CH_3)$ sym. bend. SYN enol
1367 m,sh						$\delta s(CH_3)$ + δ(OH) SYN enol
	1355 w,sh	1354 w	1355 w			δ(OH) + ν(C=O) SYN enol
	1309 mw,sh	1310 w,sh	1308 w,sh			ν(C-C=C)+ δ(OH) SYN enol
			1300 s,vbr			Luminescent band
1296 s	1296 m,br	1297mw,br	1298 ms	1296 s,br	1307 ms	ν(C-C=C)+ δ(OH) SYN enol crystal splitting
1200 w, br						δ(CH) in plane bending TS2 enol
1175 m	1173 mw	1174 m	1173 m	1176 mw	1172 m	δ(CH) in plane bending SYN enol
					1157 m	$\delta(CH_2)$ keto
			1104 w			

Additional Table 1. continued

Raman matrix 10 K enols	Raman solid 10 K enols+keto	Raman solid 10 K enols+ keto	Raman solid 10 K enols	Raman liquid 295 K enols+keto	Infrared liquid 295 K enols + keto	Assignment
		1100w vbr				Luminescent band
1040 mw	1039 w	1039 w	1039 w	1036 w	1052 w,sh	$\pi(CH_3)$ out of plane rocking SYN enol
1016 mw,sh	1025 mw	1026 w	1026 mw		1024 m	$\pi(CH_3)$ out of plane rocking SYN enol
1005 mw,sh						$\rho(CH_3)$ in plane rocking SYN enol
999 m	1001 m	1001 ms	1000 s	999 m	1003 m	$\rho(CH_3)$ in plane rocking SYN enol
	975 vw				957 m	Skeletal C-C stretch. keto
934 w	941 m	941 s	940 ms	931 mw		δ(C=C-C) + ν(C-C) SYN enol
919 w,sh	919 w	921 mw	917 w		915 ms	ν (C-CH_3) + ν(C-O) SYN enol
910 w	910 w,sh	910 mw,sh	908 mw,sh	913 w,sh		ν (C-CH_3) + ν(C-O) TS2 enol
	902 mw	904 mw	899 m			ν (C-CH_3) + ν(C-O) SYN enol crystal splitting
	817 mw	817 w				CH_2 def. keto
786 w,sh	807 w	806 w,sh				γ(CH) out of plane TS2 enol in matrix
	797 mw	797 m	798 m			γ(CH) out of plane SYN enol crystal splitting
774 w	788 w	787 w	787 mw	789 w,as	782 m,as	γ(CH) out of plane SYN enol
			770mw,br			γ(CH) out of plane TS2 enol

Additional Table 1. continued

Raman matrix 10 K enols	Raman solid 10 K enols + keto	Raman solid 10 K enols+ keto	Raman solid 10 K enols	Raman liquid 295 K enols + keto	Infrared liquid 295 K enols + keto	Assignment
					725 w,sh	
647 s	648 s	648 ms	649 s		643 mw	Out of plane ring bend.SYN enol
635 s	642 s	642 ms	643 s	645 s		In plane ring def. SYN enol
	624 mw			623 ms,sh	621 mw,sh	C-CH_2-C bending, keto tautomer
615 w,sh					583 w	In plane ring def. TS2 enol
555 mw	555 ms	554 m	554 ms	556 m		out of pl. ring def. SYN enol
	534 vw			530 vw	531 mw	C=O in plane bending, out of phase, keto tautomer
509 w	504 m	505 mw	504 m	510 vw	513 mw	in plane ring bend.SYN enol
		450 w,vbr				Luminescent band
					453 w,br	
	413 w	413 w	412 w			in plane ring def SYN enol
406 vw	404 w	406 vw	403 w	406 w		in plane ring def TS2 enol
365 vw	358 w,br	353 w	355 w,br	372 w		In plane ring defomation SYN enol
	340 w,sh			330 w		H_3C-C-C bending, keto tautomer
	235 mw	234 mw	236 mw			Out of plane ring bend.+ γ(C-CH_3) crystal splitting SYN enol
225 w			226 mw,sh	228 mw		Out of plane ring bend.+ γ(C-CH_3) SYN enol

Additional Table 1. continued

Raman matrix 10 K enols	Raman solid 10 K enols+keto	Raman solid 10 K enols+ keto	Raman solid 10 K enols	Raman liquid 295 K enols+keto	Infrared liquid 295 K enols + keto	Assignment
			203 mw,sh			Out of plane ring bend. + γ(C-CH_3) crystal splitting SYN enol
192 w	198 m	196 ms	197 m			Out of plane ring bend. + τ(CH_3) SYN enol
	174 w	170 mw	174 w			Out of plane ring bend. + τ(CH_3) SYN enol crystal splitting
158 w	155 w	153 w	155 w	160 m,sh		Methyl group torsion SYN enol (close to C-O-H)
			113 mw,sh			Lattice vibration
	101 s	101 vs	105 s			lattice vibration
	86 m,br	89 ms	90 mw			lattice vibration
	71 m	73 ms	74 m			lattice vibration
	62 vvs	63 vvs	65 vvs			Coincidence of lattice vibration and methyl group torsion SYN enol (close to C=O)
		55 ms	55 w			lattice vibration
	48 w,sh	47 m	48 w			lattice vibration
	39 w		41 w			lattice vibration
	34 w	35 m	35 w			lattice vibration
	27 w					keto lattice phonon

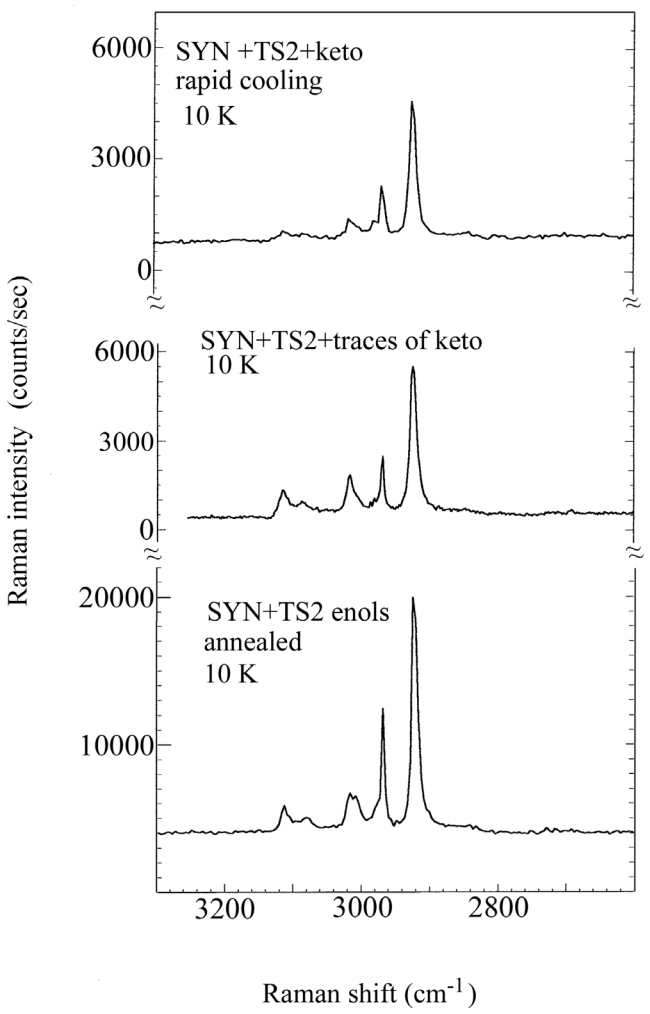
Abbreviations: v -very, s - strong, m - medium, w - weak, as - asymmetric, sh – shoulder, br - broad

Additional Table 2. Calculated unscaled frequencies for keto tautomer of acetylacetone at the B3LYP/6-31++G(d,p) level of theory[40]. The dihedral angle between two carbonyl groups was 136.48^0.

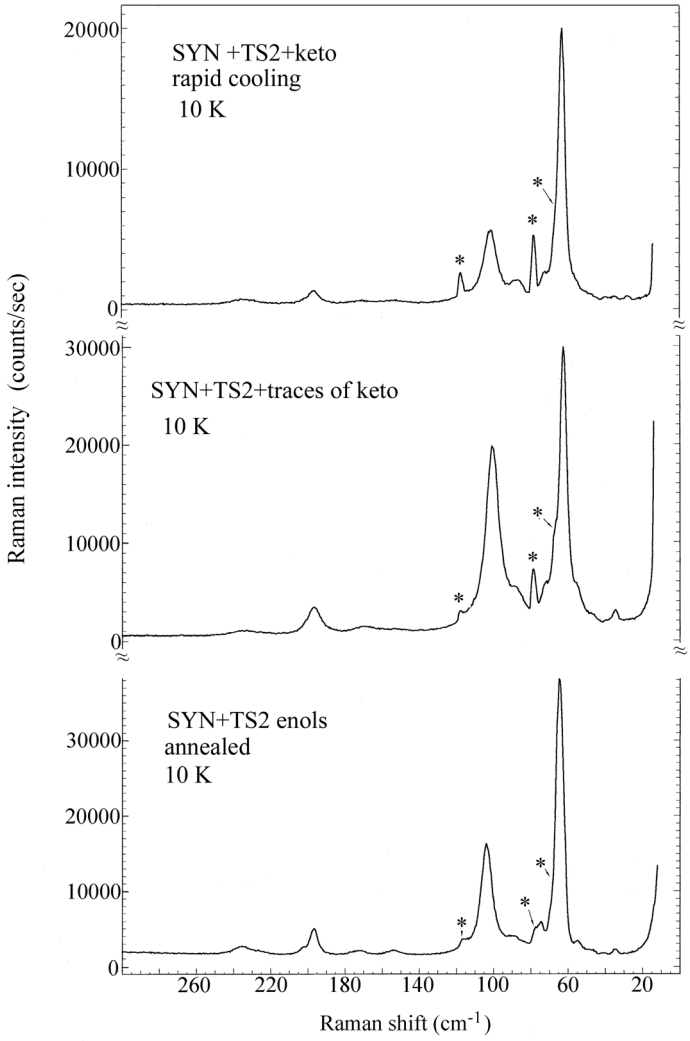
Mode no.	Harmonic frequencies (unscaled) (cm^{-1})	Infrared intensity (KM/mole)	Raman scattering activity ($10^{-40}m^4$/a.m.u.)
1	3163	7.6	70.0
2	3158	8.1	72.2
3	3149	5.4	48.9
4	3111	2.8	47.7
5	3107	3.0	48.4
6	3081	3.0	102.0
7	3042	1.5	172.7
8	3041	2.0	100.6
9	1799	23.3	16.0
10	1770	384.0	4.6
11	1486	10.0	4.5
12	1481	8.2	10.3
13	1476	10.1	9.7
14	1468	26.4	4.2
15	1464	9.1	12.3
16	1394	35.8	1.75
17	1390	55.4	1.2
18	1268	26.1	4.1
19	1260	98.8	0.3
20	1187	193.6	1.0
21	1145	1.35	8.5
22	1079	0.4	0.3
23	1061	8.6	0.3

Additional Table 2. continued.

Mode no.	Harmonic frequencies unscaled (cm^{-1})	Infrared intensity (KM/mole)	Raman scattering activity ($10^{-40}m^4$/a.m.u.)
24	1003	0.6	0.1
25	942	1.2	4.2
26	900	26.1	1.9
27	800	12.1	3.3
28	785	0.2	14.2
29	626	1.4	9.3
30	544	25.1	0.7
31	500	1.1	0.4
32	484	6.0	2.5
33	411	2.0	0.1
34	320	0.8	1.0
35	167	0.1	0.3
36	150	0.3	1.3
37	142	1.0	1.0
38	55	9.3	1.2
39	39	11.8	0.5



Additional Figure 1. Low temperature Raman spectra of polycrystalline acetylacetone at 10 K obtained when the sample was cooled rapidly from room temperature to 10 K (spectrum at the top), when the sample was cooled to 185 K, heated above the solid-solid phase transition temperature to 230 K and then cooled to 10 K (middle spectrum), and for annealed sample (spectrum at the bottom) (2600 cm^{-1}- 3300 cm^{-1}).



Additional Figure 2. Low temperature Raman spectra of polycrystalline acetylacetone at 10 K obtained when the sample was cooled rapidly from room temperature to 10 K (spectrum at the top), when sample was cooled to 185 K, heated above the solid-solid phase transition temperature to 230 K and then cooled to 10 K (middle spectrum), and for annealed sample (spectrum at the bottom) (10 cm^{-1} - 300 cm^{-1}). Asterisks denote laser plasma lines.