Table S1. Calculated energies (kJ mol^{-1}) for the relevant conformations of methyl cyanoacetate.

	syn	$TS_{(syn \rightarrow gauche)}$	*gauche*	$TS_{(gauche \rightarrow gauche)}$
B3LYP/6-31G*	-946805.334		-946806.051	
B3LYP/6-31G*+ZPVE' [a]	-946571.105 (0.000)		-946570.900 (0.205)	
$h\nu_{C-C}/2$	0.191		0.126	
ΔE_{ZPVE}	0.000		0.140	
MP2/6-31G**	-944165.739	-944162.717	-944166.292	-944165.382
MP2/6-31G** +ZPVE' [a]	-943928.048 (0.000)	-943924.264 (3.784)	-943927.939 (0.109)	-943927.538 (0.510)
$h\nu_{C-C}/2$	0.140		0.205	
ΔE_{ZPVE}	0.000	3.644[b]	0.174	0.370[c]

[a] ZPVE' corresponds to the total zero-point vibrational energy *minus* the contribution associated with the C-C torsion ($h\nu_{C-C}/2$). Values in parentheses are relative energies to the conformational ground state.

[b] Value relative to the *gauche* conformer, corresponding to the energy barrier of conversion of the *gauche* forms to the *syn* conformer is 3.470 kJ mol^{-1}.

[c] Value relative to the *gauche* conformer, corresponding to the energy barrier of interconversion between the two degenerated-by-symmetry *gauche* forms is 0.196 kJ mol^{-1}.

Table S2. MP2/6-31G** and B3LYP/6-31G* calculated geometries for the relevant conformations of methyl cyanoacetate.[a]

Parameter	*syn*		$TS_{(syn \rightarrow gauche)}$		*gauche*		$TS_{(gauche \rightarrow gauche)}$	
	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP
Bond lengths*/pm*								
C=O	121.48	120.57	121.58	120.67	121.67	120.86	121.71	120.86
C-O	135.07	134.60	134.78	134.29	134.56	133.78	134.35	133.74
C1-C5	152.11	153.08	152.34	153.52	152.18	153.24	152.27	153.25
O-C	144.40	144.17	144.49	144.25	144.43	144.18	144.46	144.19
C-H8	108.66	109.26	108.66	109.26	108.67	109.27	108.66	109.26
C-H9	108.66	109.26	108.65	109.25	108.65	109.25	108.66	109.26
C-H10	108.36	108.97	108.35	108.96	108.34	108.94	108.33	109.93
C5-C6	146.05	146.12	146.39	146.44	146.27	146.23	146.15	146.22
C-H11	109.07	109.67	108.99	109.58	108.81	109.50	109.06	109.63
C-H12	109.07	109.67	108.79	109.38	109.19	109.76	109.06	109.63
CN	117.99	115.93	118.05	116.00	118.04	115.99	118.02	116.00
Bond angles*/degrees*								
O=CO	125.15	125.18	125.24	125.26	125.26	125.40	125.33	125.41
C-C=O	126.09	125.96	124.36	124.25	123.94	122.17	122.46	121.99
C-C-O	108.76	108.86	110.40	110.49	110.76	112.41	112.22	112.60
C-O-C	113.86	115.28	113.80	115.20	114.12	115.53	114.03	115.54
O-C-H8	110.20	110.33	110.14	110.29	110.14	110.24	110.09	110.24
O-C-H9	110.20	110.33	110.06	110.19	110.10	110.23	110.09	110.24
O-C-H10	105.04	105.38	105.02	105.38	104.97	105.29	104.92	105.29
H8-C-H9	109.37	109.21	109.42	109.26	109.46	109.29	109.45	109.28
H8-C-H10	110.99	110.77	111.06	110.85	111.07	110.87	111.11	110.87
H9-C-H10	110.99	110.77	111.06	110.83	111.02	110.86	111.11	110.87
C-C-C	112.31	113.15	110.11	111.38	113.33	116.15	115.43	116.39
C1-C-H11	108.72	108.73	107.98	107.75	107.82	107.29	107.35	107.20
C1-C-H12	108.72	108.73	110.51	110.46	108.04	107.22	107.35	107.20
C6-C-H11	110.09	109.91	109.06	108.89	110.38	110.03	109.84	109.70
C6-C-H12	110.09	109.91	109.81	109.57	109.06	109.36	109.84	109.70
H11-C-H12	106.75	106.16	109.34	108.72	108.06	106.32	106.63	106.13
C-CN	178.28	178.18	179.63	189.37	178.62	178.47	177.97	178.30
Out-of-plane and dihedral angles*/degrees*								
N ∠C-C-C[b]	0.00	0.00	0.16	0.26	-0.34	-0.16	0.00	0.00
O=C-O-C	0.00	0.00	0.69	0.83	1.22	0.44	0.00	0.00
C-C-O-C	180.00	180.00	-179.04	-179.50	178.83	178.91	180.00	180.00
O=C-C-C	0.00	0.00	-70.48	-68.85	-139.94	-166.91	180.00	180.00
O=C-C-H11	122.07	122.41	48.49	50.52	-17.47	-43.38	-57.16	-56.80
O=C-C-H12	-122.07	-122.41	168.03	169.14	99.10	70.48	57.16	56.80
C-O-C-H8	-60.39	-60.38	-60.45	-60.14	-61.60	-60.92	-60.38	-60.37
C-O-C-H9	60.39	60.38	60.28	60.56	59.20	59.82	60.38	60.37
C-O-C-H10	180.00	180.00	179.90	-179.83	178.76	179.44	180.00	180.00

[a] See Figure 1 for atom numbering.
[b] Nitrogen atom out-of-the-plane defined by the carbon atoms.

Table S3. Experimental and calculated (B3LYP/6-31G*) wavenumbers and intensities and band assignments for methyl cyanoacetate (conformational ground state: *syn*). [a]

	B3LYP/6-31G*			Experiment (Argon)				Experiment (Xenon)			
	ν	I	fitted[b]	ν	I	ν_{gc}	I_{gc}	ν	I	ν_{gc}	I_{gc}
ν CH_3 as A'	3189.7	13.2	3051.3	3046.0		3046.0	0.138[d]	3032.2		3032.2	0.146[d]
ν CH_3 as A"	3160.1	17.0	3023.2	3016.4		3014.8[c]	0.236[d]	2998.4		2998.4	0.232[d]
				3013.3							
ν CH_2 as	3106.4	0.01	2972.3	2986.6		2986.6	0.014[d]	2968.8		2968.8	<0.001[d]
ν CH_3 s	3081.7	23.9	2948.9	2969.0		2967.3[c]	0.454[d]	2950.1		2950.1	0.346[d]
				2967.2							
				2965.7							
ν CH_2 s	3069.3	2.5	2937.1	2942.9		2942.9	0.012	2932.9		2932.9	0.075[d]
ν CN	2390.2	3.6	2293.3	2256.9		2256.9	0.009	2258.3		2258.3	0.015
ν C=O	1852.9	198.2	1783.8	1783.1	0.324	1779.3	0.999	1779.6	0.173	1771.0	1.269
				1777.5	0.675			1769.7	1.096		
δ CH_3 as A'	1523.9	9.7	1471.9	1459.8		1459.8	0.094	1454.6		1454.6	0.082
δ CH_3 as A"	1511.8	7.2	1460.4	1454.3		1454.3	0.019[d]	1450.9		1450.9	0.059[d]
δ CH_3 s	1492.6	10.2	1442.2	1441.0		1441.0	0.275	1436.9		1436.9	0.562[d]
δ CH_2	1470.1	17.5	1420.9	1405.7		1405.7	0.181	1401.4	0.093	1397.8	0.193
								1398.4	0.022		
								1394.1	0.034		
								1392.8	0.044		
ω CH_2	1375.8	107.8	1331.5	1354.6	0.177	1341.8	1.237	1348.1	0.099	1338.6	0.842
				1346.0	0.460			1347.0	0.048		
				1339.7	0.241			1344.3	0.151		
				1331.7	0.359			1335.8	0.345		
								1332.4	0.199		
ν C1-O3	1236.3	314.9	1199.2	1206.3	0.286	1201.6	1.860	1211.9	0.114	1202.0	1.105
				1201.5	1.573			1204.2	0.319		
								1200.8	0.325		
								1199.2	0.143		
								1197.2	0.204		
tw CH_2	1234.6	0.1	1197.6	n.obs				n.obs		n.obs	
γ CH_3 A'	1211.0	77.9	1175.3	1181.1		1181.1	1.094	1179.8		1179.8	0.801
γ CH_3 A"	1186.0	1.0	1151.6	1159.6		1159.6	0.017	1163.4		1163.4	<0.001
ν O3-C4	1042.0	17.7	1015.0	1022.7		1020.5[c]	1.330[d]	1014.7		1014.7	0.927[d]
				1019.0							
γ CH_2	968.1	6.8	945.0	936.8		936.8	0.040	941.2	0.013	939.8	0.033
								938.9	0.020		
ν C5-C6	956.6	7.0	934.1	934.9	0.054	934.0	0.083	935.7		935.7	0.026
				932.4	0.029						
ν C1-C5	906.9	6.2	886.9	889.5		889.5	0.041	892.2		892.2	0.053
δ OCO	715.9	11.2	705.8	707.1		707.1	0.086	715.7	0.036	711.4	0.138
								709.9	0.102		
γ C=O	583.4	4.7	580.2	577.5		577.5	0.035	574.8		574.8	0.030
δ CCN	458.5	0.8	461.8								
δ CC=O	383.3	10.8	390.5								
γ CCN	365.1	1.0	373.3								
δ COC	279.0	10.1	291.6								
τ C1-O3	167.8	10.0	186.2								
τ CH_3	135.5	1.9	155.6								
δ CCC	105.5	0.1	127.1								
τ C-C	31.8	3.1	57.2								

[a] Wavenumbers in cm^{-1}; calculated intensities in km mol^{-1}; experimental intensities are integrated intensities measured in the spectrum resulting from deposition at 10 K (Ar) or 20 K (Xe) with the valve nozzle at *ca.* 293 K. ν, stretching; δ, bending; ω, wagging; tw, twisting; γ, rocking; τ, torsion. $\nu_{gc}= \Sigma(I_i\nu_i)/\Sigma I_i$, is the wavenumber of the gravity centre of the absorptions due to the same vibration; $I_{gc}= \Sigma I_i$.

[b] Fitted wavenumbers were obtained by linear regression, using the experimental bands (gravity centres) observed in argon and B3LYP calculated values. The equation resulting from the regression (R^2= 0.999845; mean error= 0.5%) is $\nu_{fitted}= 0.9481\ \nu_{B3LYP}+27.1$.

[c] Intensities of individual component bands could not be measured. ν_{gc} corresponds to the average frequency of the components.

[d] This band contains contributions due to the two observed conformers. The value I_{gc} here presented corresponds to the total intensity.

Table S4. Experimental and calculated (B3LYP/6-31G*) wavenumbers and intensities and band assignments for methyl cyanoacetate (first excited conformational state). [a]

	B3LYP/6-31G*							Experiment (Argon)				Experiment (Xenon)			
	gauche			*TS(gauche→gauche)*											
	ν	I	fitted[b]	ν	I	fitted[b]	Δν[c]	ν	I	ν_{gc}	I_{gc}	ν	I	ν_{gc}	I_{gc}
ν CH_3 as A'	3195.6	10.6	3056.9	3195.3	10.2	3056.6	-0.3	3046.0		3046.0	0.138[d]	3032.2		3032.2	0.146[d]
ν CH_3 as A"	3161.3	16.8	3024.3	3161.8	16.9	3024.8	0.5	3020.3		3020.3	0.236[d]	2998.4		2998.4	0.232[d]
ν CH_2 as	3118.6	0.2	2983.9	3111.0	0.1	2976.7	-7.6	2986.6		2986.6	0.014[d]	2968.8		2968.8	<0.001[d]
ν CH_3 s	3083.1	22.9	2950.2	3083.5	22.8	2950.6	0.4	2970.1		2965.3[e]	0.454[d]	2950.1		2950.1	0.346[d]
								2964.2							
								2961.7							
ν CH_2 s	3075.8	1.5	2943.3	3074.1	1.5	2941.7	-1.7	2947.4		2947.4	0.011	2932.9		2932.9	0.075[d]
ν CN	2381.5	6.3	2285.0	2383.1	5.6	2286.5	1.6	2279.8		2279.8	0.035	2278.2		2278.2	0.019
ν C=O	1839.3	266.4	1770.9	1838.4	270.4	1770.1	-0.9	1770.5	2.160	1769.4	4.860	1761.6	2.401	1761.4	2.457
								1768.5	2.700			1751.5	0.056		
δ CH_3 as A'	1521.7	8.7	1469.8	1521.6	8.6	1469.7	-0.1	1459.1		1459.1	0.094	1453.1		1453.1	0.046
δ CH_3 as A"	1515.5	7.7	1464.0	1511.5	7.8	1460.2	-4.0	1454.3		1454.3	0.019[d]	1450.9		1450.9	0.059[d]
δ CH_3 s	1495.1	9.3	1444.6	1491.4	9.8	1441.1	-3.7	1441.6		1441.6	0.304	1436.9		1436.9	0.562[d]
δ CH_2	1473.4	8.2	1424.0	1468.6	6.4	1419.5	-4.8	1403.5		1403.5	0.137	1399.5	0.071	1397.8	0.153
												1396.4	0.082		
ω CH_2	1339.8	1.5	1297.4	1340.4	4.0	1297.9	0.6	1300.8	0.080	1299.9	0.168	1304.7	0.060	1296.4	0.207
								1299.1	0.088			1295.8	0.098		
												1287.4	0.049		
ν C1-O3	1306.6	352.2	1265.9	1302.4	396.0	1261.9	-4.2	1271.2	2.330	1269.8	5.103	1270.9	0.092	1263.3	2.880
								1268.6	2.773			1265.4	0.684		
												1262.3	2.104		
tw CH_2	1234.0	43.6	1197.1	1247.1	0.2	1209.5	13.1	1212.2		1212.2	<0.001	1208.3		1208.3	0.197
γ CH_3 A'	1219.2	4.3	1183.0	1215.3	3.1	1179.3	-3.9	1196.4	0.010	1194.8	0.018	1188.2		1188.2	0.016
								1192.8	0.008						
γ CH_3 A"	1185.8	1.1	1151.4	1184.7	1.1	1150.3	-1.1	1165.8		1165.8	0.015	1157.1		1157.1	0.016
ν O3-C4	1045.2	39.9	1018.1	1042.5	39.2	1015.5	-2.7	1023.8		1021.4[e]	1.330[d]	1014.7		1014.7	0.927[d]
								1019.0							
ν C5-C6	986.6	1.2	962.5	990.4	0.4	966.1	3.8	n.obs				944.3		944.3	0.009
γ CH_2	961.4	4.4	938.6	964.6	7.8	941.6	3.2	934.0	0.054	933.2	0.083	932.9	0.026	930.9	0.215
								931.7	0.029			930.6	0.189		
ν C1-C5	860.7	20.1	843.1	860.0	21.1	842.5	-0.7	847.9	0.377	847.7	0.440	844.2		844.2	0.269
								846.4	0.063						
δ OCO	719.4	7.4	709.2	686.0	6.9	677.5	-33.4	683.7		683.7	0.043	685.9	0.071	685.1	0.095
												682.6	0.024		
γ C=O	589.3	7.1	585.8	597.1	5.6	593.2	7.8	591.6		591.6	0.078	587.9		587.9	0.085
δ CCN	487.6	3.3	489.4	495.2	3.7	496.6	7.6								
δ CC=O	386.8	3.3	393.8	382.5	4.1	389.8	-4.3								
γ CCN	362.1	1.8	370.4	364.1	1.0	372.3	2.0								
δ COC	281.1	15.5	293.6	283.6	15.9	296.0	2.5								
τ C1-O3	190.4	9.5	207.6	178.3	8.6	196.1	-12.1								
τ CH_3	134.5	1.0	154.6	130.6	4.7	150.9	-3.9								
δ CCC	120.7	4.2	141.5	86.7	0.8	109.3	-34.0								
τ C-C	21.0	9.3	47.0												

[a] Wavenumbers in cm^{-1}; calculated intensities in km mol^{-1}; experimental intensities are integrated intensities measured in the spectrum resulting from deposition at 10 K (Ar) or 20 K (Xe) with the valve nozzle at *ca.* 293 K. ν, stretching; δ, bending; ω, wagging; tw, twisting; γ, rocking; τ, torsion.
$\nu_{gc}=\Sigma(I_i\nu_i)/\Sigma I_i$, is the wavenumber of the gravity centre of the absorptions due to the same vibration; $I_{gc}=\Sigma I_i$.
[b] Fitted wavenumbers were obtained by linear regression, using the experimental bands (gravity centres) observed in argon and B3LYP calculated values. The equation resulting from the regression (R^2= 0.999845; mean error= 0.5%) is $\nu_{fitted}= 0.9481\ \nu_{B3LYP}+27.1$.
[c] $\Delta\nu=\nu_{TS(gauche\rightarrow gauche)}-\nu_{gauche}$.

[d] This band contains contributions due to the two observed conformers. The value I_{gc} here presented corresponds to the total intensity.
[e] Intensities of individual component bands could not be measured. ν_{gc} corresponds to the average frequency of the components.