Supplementary Material

Table S1
Definition of Internal Symmetry Coordinates Used in the Normal Mode Analysis of the Conformations of Dimethyl Oxalate.

coordinate	approximate description	symmetry		definition [b]
		C_{2h}	C_2	
S_1	νC-C	A_g	A	$\nu_{2,4}$
S_2	νC=O	A_g	A	$\nu_{1,2} + \nu_{3,4}$
S_3	νC=O	B_u	B	$\nu_{1,2} - \nu_{3,4}$
S_4	νC-O	A_g	A	$\nu_{4,6} + \nu_{2,5}$
S_5	νC-O	B_u	B	$\nu_{4,6} - \nu_{2,5}$
S_6	νO-CH_3	A_g	A	$\nu_{5,7} + \nu_{6,11}$
S_7	νO-CH_3	B_u	B	$\nu_{5,7} - \nu_{6,11}$
S_8	νCH_3 sym	A_g	A	$\nu_{7,10} + \nu_{7,8} + \nu_{7,9} + \nu_{11,13} + \nu_{11,12} + \nu_{11,14}$
S_9	νCH_3 sym	B_u	B	$\nu_{7,10} + \nu_{7,8} + \nu_{7,9} - \nu_{11,13} - \nu_{11,12} - \nu_{11,14}$
S_{10}	νCH_3 asym	A_g	A	$2\nu_{7,10} - \nu_{7,8} - \nu_{7,9} + 2\nu_{11,13} - \nu_{11,12} - \nu_{11,14}$
S_{11}	νCH_3 asym	B_u	B	$2\nu_{7,10} - \nu_{7,8} - \nu_{7,9} - 2\nu_{11,13} + \nu_{11,12} + \nu_{11,14}$
S_{12}	νCH_3 asym'	A_u	A	$\nu_{7,8} - \nu_{7,9} + \nu_{11,12} - \nu_{11,14}$
S_{13}	νCH_3 asym'	B_g	B	$\nu_{7,8} - \nu_{7,9} - \nu_{11,12} + \nu_{11,14}$
S_{14}	δCH_3 sym	A_g	A	$\delta_{8,9,7} + \delta_{9,10,7} + \delta_{8,10,7} - \delta_{8,5,7} - \delta_{9,5,7} - \delta_{10,5,7} + \delta_{12,14,11} + \delta_{12,13,11} + \delta_{13,14,11} - \delta_{12,6,11} - \delta_{13,6,11} - \delta_{14,6,11}$
S_{15}	δCH_3 sym	B_u	B	$\delta_{8,9,7} + \delta_{9,10,7} + \delta_{8,10,7} - \delta_{8,5,7} - \delta_{9,5,7} - \delta_{10,5,7} - \delta_{12,14,11} - \delta_{12,13,11} - \delta_{13,14,11} + \delta_{12,6,11} + \delta_{13,6,11} + \delta_{14,6,11}$
S_{16}	δCH_3 asym	A_g	A	$2\delta_{8,9,7} - \delta_{9,10,7} - \delta_{8,10,7} + 2\delta_{12,14,11} - \delta_{12,13,11} - \delta_{13,14,11}$
S_{17}	δCH_3 asym	B_u	B	$2\delta_{8,9,7} - \delta_{9,10,7} - \delta_{8,10,7} - 2\delta_{12,14,11} + \delta_{12,13,11} + \delta_{13,14,11}$
S_{18}	δCH_3 asym'	B_g	B	$\delta_{9,10,7} - \delta_{8,10,7} + \delta_{12,13,11} - \delta_{13,14,11}$
S_{19}	δCH_3 asym'	A_u	A	$\delta_{9,10,7} - \delta_{8,10,7} - \delta_{12,13,11} + \delta_{13,14,11}$
S_{20}	γCH_3	A_g	A	$2\delta_{10,5,7} - \delta_{9,5,7} - \delta_{8,5,7} + 2\delta_{13,6,11} - \delta_{12,6,11} - \delta_{14,6,11}$
S_{21}	γCH_3	B_u	B	$2\delta_{10,5,7} - \delta_{9,5,7} - \delta_{8,5,7} - 2\delta_{13,6,11} + \delta_{12,6,11} + \delta_{14,6,11}$
S_{22}	γCH_3'	B_g	B	$\delta_{9,5,7} - \delta_{8,5,7} + \delta_{12,6,11} - \delta_{14,6,11}$
S_{23}	γCH_3'	A_u	A	$\delta_{9,5,7} - \delta_{8,5,7} - \delta_{12,6,11} + \delta_{14,6,11}$
S_{24}	τCH_3	B_g	B	$\tau_{10,7,5,2} + \tau_{9,7,5,2} + \tau_{8,7,5,2} - \tau_{13,11,6,4} - \tau_{14,11,6,4} - \tau_{12,11,6,4}$
S_{25}	τCH_3	A_u	A	$\tau_{10,7,5,2} + \tau_{9,7,5,2} + \tau_{8,7,5,2} + \tau_{13,11,6,4} + \tau_{14,11,6,4} + \tau_{12,11,6,4}$
S_{26}	δCCO	A_g	A	$\delta_{2,6,4} + \delta_{4,5,2}$
S_{27}	δCCO	B_u	B	$\delta_{2,6,4} - \delta_{4,5,2}$
S_{28}	δCC=O	A_g	A	$\delta_{1,4,2} + \delta_{3,2,4}$
S_{29}	δCC=O	B_u	B	$\delta_{1,4,2} - \delta_{3,2,4}$
S_{30}	δCOC	A_g	A	$\delta_{4,11,6} + \delta_{2,7,5}$
S_{31}	δCOC	B_u	B	$\delta_{4,11,6} - \delta_{2,7,5}$
S_{32}	τC-O	A_u	A	$\tau_{7,5,2,4} + \tau_{11,6,4,2}$
S_{33}	τC-O	B_g	B	$\tau_{7,5,2,4} - \tau_{11,6,4,2}$
S_{34}	τC-C	A_u	A	$\tau_{1,2,4,3} + \tau_{1,2,4,6} + \tau_{5,2,4,6} + \tau_{5,2,4,3}$
S_{35}	γC=O	A_u	A	$\tau_{1,2,4,5} + \tau_{3,4,2,6}$
S_{36}	γC=O	B_g	B	$\tau_{1,2,4,5} - \tau_{3,4,2,6}$

[a] ν - stretching; δ - bending; γ - rocking; τ - torsion.

[b] $\nu_{i,,j}$ is the distance between atoms A_i and $A_{j;}$ $\delta_{i,k,j}$ is the angle between vectors A_iA_j and A_jA_k; $\tau_{i,j,k,l}$ is the dihedral angle between the plane defined by A_i, A_j, A_k and the plane defined by A_j, A_k, A_l atoms (see Scheme 1 for atom numbering).

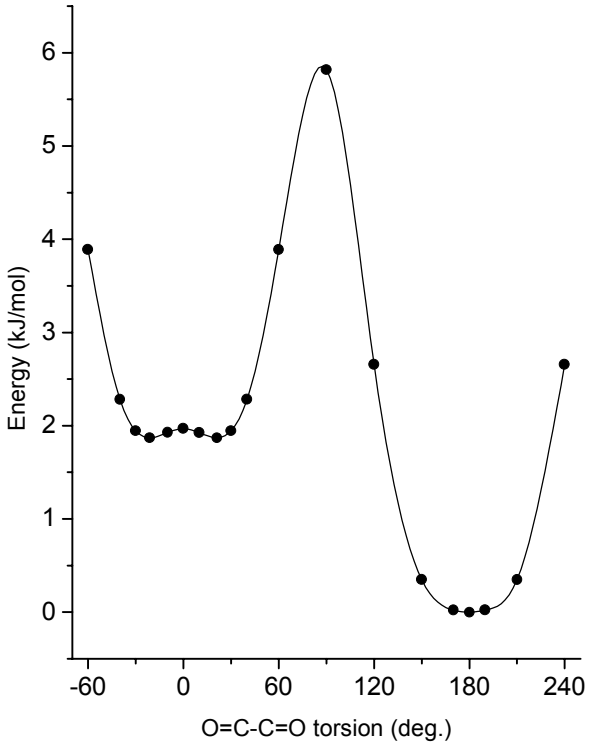
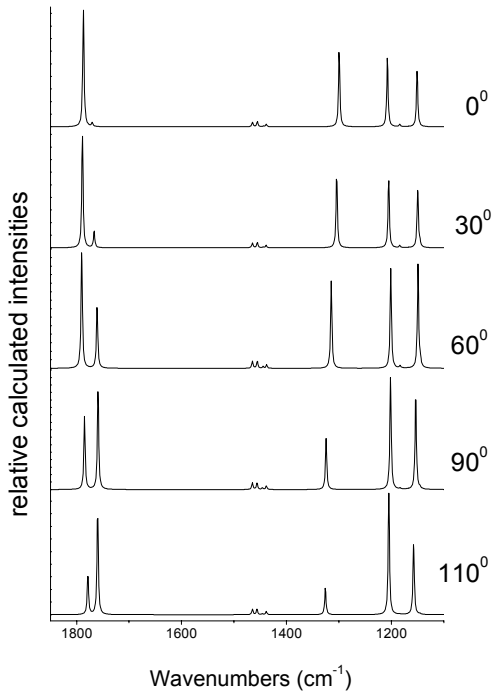


Fig. S1. Electronic energy of DMO calculated at MP2/6-31G** level as a function of O=C-C=O torsion.



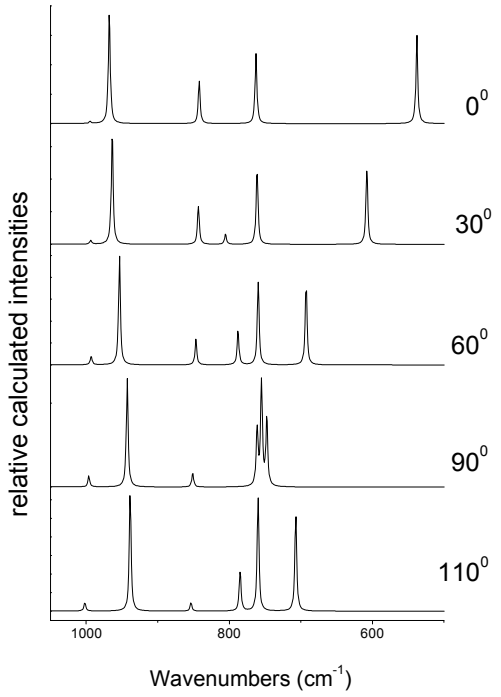


Fig. S2. Theoretical (DFT(B3LYP)/6-31++G**) spectra of a series of conformations of DMO corresponding to O=C-C=O torsional angles 110 – 0^{o}. The calculated frequencies were scaled down by a factor 0.978.