UNUSIALLY HIGH SPIN-ORBIT COUPLING IN THE METHIONINE SINGLET-TRIPLET TRANSITION AND THE ROLE OF MAGNETIC PERTURBATIONS IN AMINO ACIDS

B. Minaev *[a,b], M. Sukhyna [a], P. Stakhira [d], V. Minaeva [a], H. Agren [b,c]

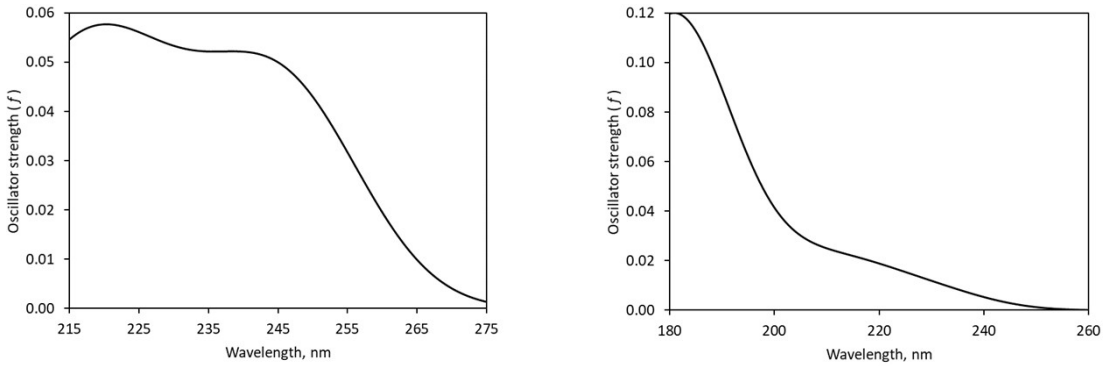
Supplementary Information

Table S1. Optimized bond lengths (Å) of L-methionine in the ground S_0 state and in the triplet excited T_1 state

State	C1–N2	C1–C3	C3–C4	C4–S5	S5–C6	C1–C7	C7=O8	C7–O9
S_0	1.456	1.548	1.530	1.832	1.828	1.530	1.206	1.356
T_1	1.480	1.545	1.528	1.796	1.801	1.521	1.271	1.467

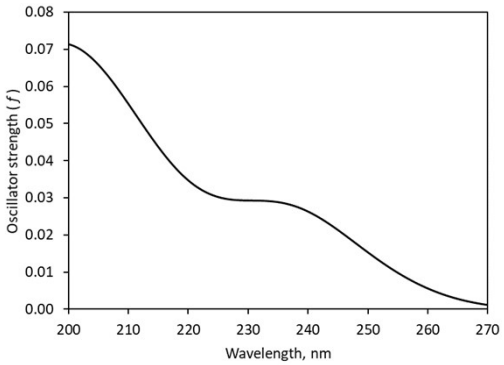
Table S2. Some important dihedral and valence angles in the S_0 and T_1 states of methionine

Angle	State S_0	State T_1
O8–C7–C1	125.35°	117.90°
O8=C7–C1–C3	103.34°	176.71°
C1–C3–C4–S5	175.52°	164.84°
C7–C1–C3–C4	171.42°	-173.96°
C3–C4–S5–C6	71.78°	-44.74°
O8=C7–O9–H20	-1.15°	-19.52°
C4–S5–C6	101.110°	105.33°

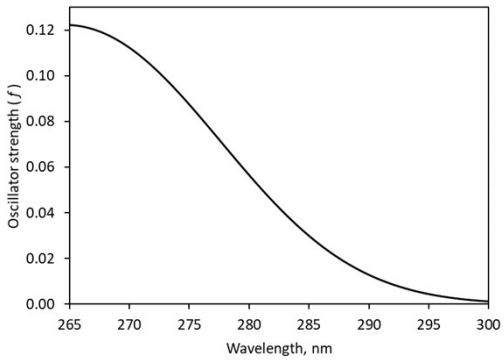


(a) (b)

[a] Cherkasy National University named after Bogdan Khmelnytsky, Institute of Natural and Agricultural Sciences, Cherkasy, Cherkasy Oblast, UA.
[b] Uppsala Universitet, Department of Physics and Astronomy, Uppsala, Uppsala County, SE.
[c] Wroclaw University of Science and Technology, Faculty of Chemistry, Wrocław, PL-50370, PL.
[d] Lviv Polytechnic National University Institute of Telecommunications Radioelectronics and Electronic Engineering, Department of Electronic Engineering, Lviv, Lviv Oblast, UA.



(c)



(d)

Figure S1. Electronic spectrum of (a – L-methionine, b – glycine, c – cysteine, d – tryptophane) in the TD-DFT approximation (Gaussian broadening, Band width on 1/2 height = 0.61 eV)

Table S3. A comparative characterization of amino acids triplet state

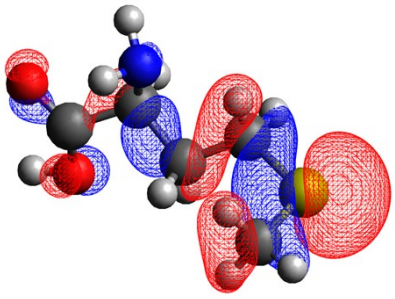
Amino acid	$\langle T_1\|H_{SO}\|S_0\rangle$, cm^{-1}	$f_{S_0 \to T_1}$	$\tau(T_1)$, s	$\Delta E_{vert}(S_0–T_1)$, eV	State	Dipole moment (a.u.)		
						x	y	z
Methionine	116.7	$2.81 \cdot 10^{-6}$	0.000362	4.757	S_0	-0.51999	-0.93220	-0.11037
					T_1	-1.99704	2.61092	5.47065
Glycine	16.90	$4.90 \cdot 10^{-8}$	0.0165	5.176	S_0	-0.41781	-0.35287	0.62566
					T_1	0.37665	0.56180	-0.22223
Cysteine	90.87	$4.00 \cdot 10^{-6}$	0.00027	4.621	S_0	-0.15473	-0.52251	0.67677
					T_1	-0.84266	-0.69825	0.49635
Tryptophane	0.679	$2.60 \cdot 10^{-8}$	0.079	3.350	S_0	1.16436	0.27871	1.04786
					T_1	1.80283	1.45355	-1.01993

Table S4. Optimized bond lengths (Å) of glycine in the ground S_0 state and in the triplet excited T_1 state

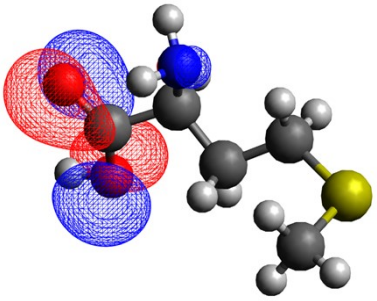
State	C–O	C=O	C–C	C–N	C–H1	C–H3	O–H	N–H5	N–H6
S_0	1.353	1.205	1.512	1.455	1.104	1.094	0.969	1.013	1.015
T_1	1.416	1.276	1.617	1.418	1.087	1.094	0.965	1.014	1.014

Table S5. Optimized bond lengths (Å) of cysteine in the ground S_0 state and in the triplet excited T_1 state

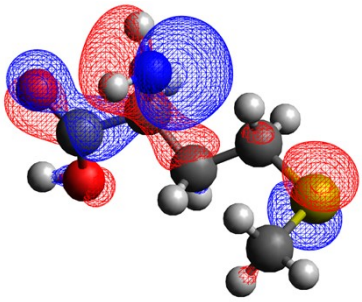
State	C2–C6	C2–C8	C8=O9	C8–O10	O10–H	C2–N3	C6–S12	S12–H
S_0	1.544	1.543	1.199	1.359	0.966	1.455	1.834	1.350
T_1	1.533	1.502	1.360	1.382	0.965	1.477	1.852	1.348



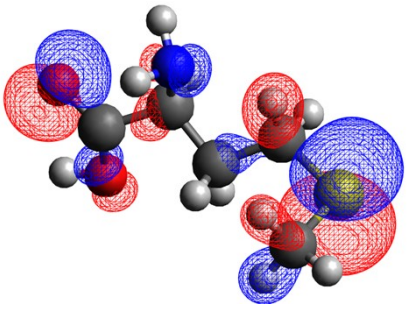
36 (HOMO–4)
E = –9.213 eV



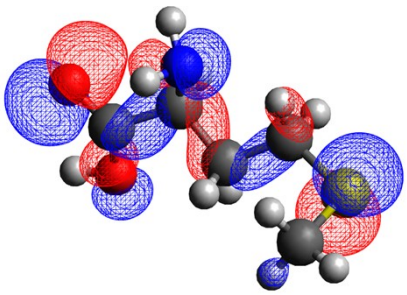
37 (HOMO–3)
E = –8.797 eV



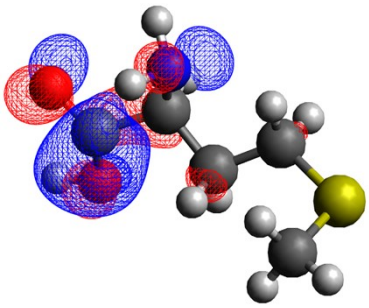
38 (HOMO–2)
E = –8.509 eV



39 (HOMO–1)
E = –7.747 eV

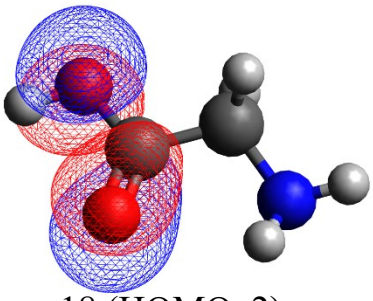


40 (HOMO)
E = –6.744 eV

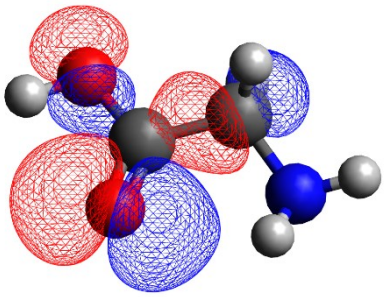


41 (LUMO)
E = –3.991 eV

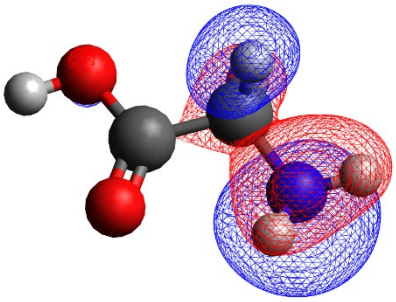
Figure S2. Molecular orbitals of methionine at the T_1 state geometry obtained by TD-TDF method



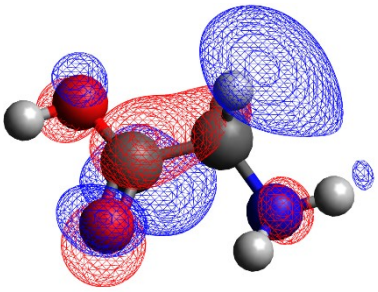
18 (HOMO–2)
π_y-type (O–C=O) (E = –9.265 eV)



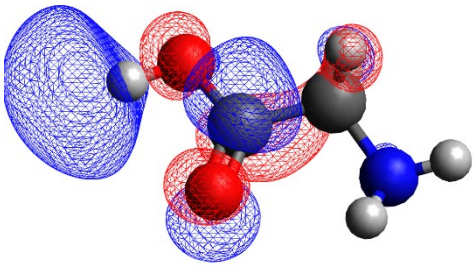
19 (HOMO–1)
n-type (p_z)(C=O) (E = –8.128 eV)



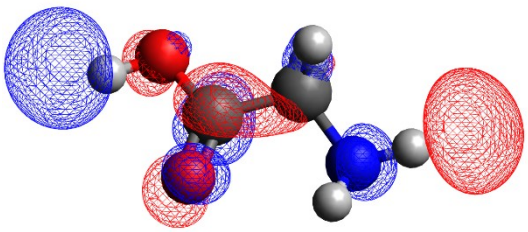
20 (HOMO)
$n_{N\text{-type}}(p_y)$ (E = –6.868 eV)



21 (LUMO)
π_y*-type (C=O) (E = –0.502 eV)

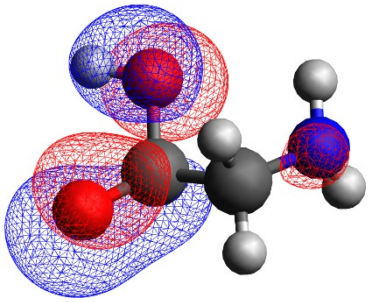


22 (LUMO+1)
$\pi_y{}^*_{C=O}$ σ^*_{O-H} (E = –0.235 eV)

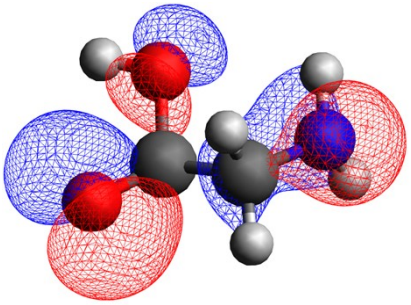


22 (LUMO+2)
(E = 0.010 eV)

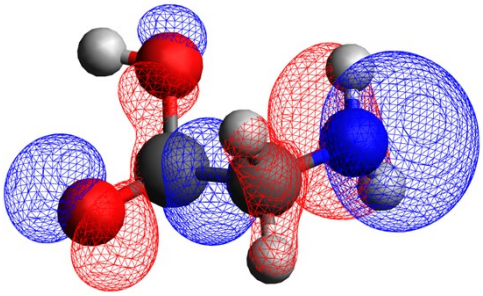
Figure S3. Molecular orbitals of glycine at the S_0 state geometry



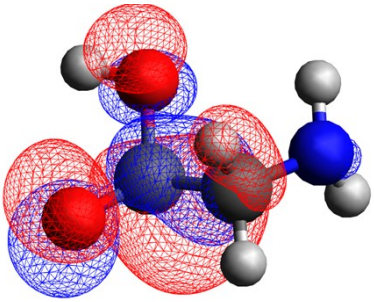
18 (HOMO–2)
π-type (O–C=O) E = –8.962 eV



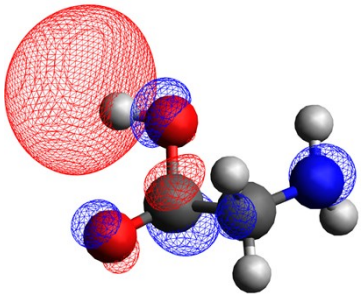
19 (HOMO–1)
n(C=O, N)-type (E = –8.345 eV)



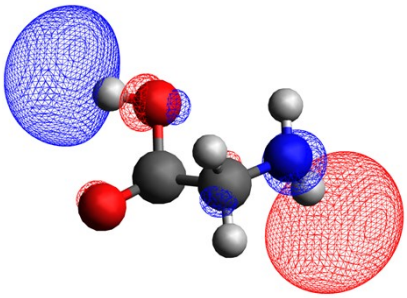
20 (HOMO)
π(N)-type E = –6.402 eV



21 (LUMO)
π(C=O)-type E = –2.519 eV

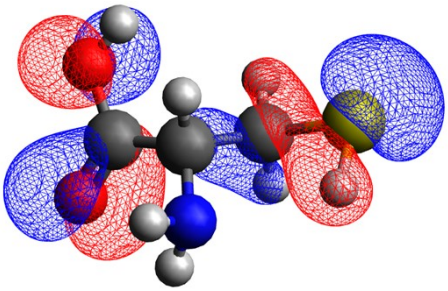


22 (LUMO+1)
σ(O–H), n(N)-type E = –0.227 eV

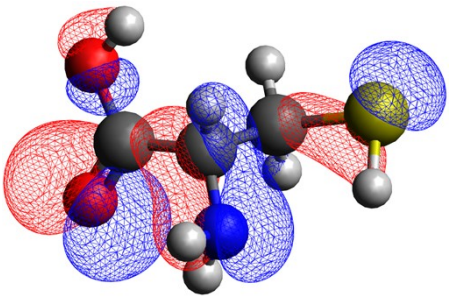


22 (LUMO+2)
σ(O–H, N–H)-type, E = 0.151 eV

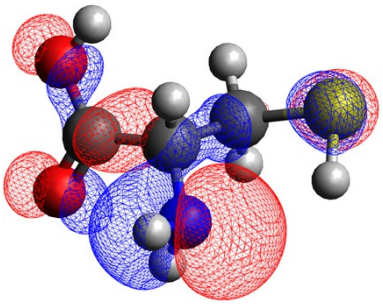
Figure S4. Molecular orbitals of glycine at the T_1 state geometry obtained by TD-TDF method



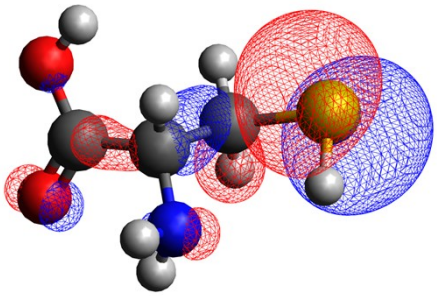
29 (HOMO–3)
E = –9.299 eV



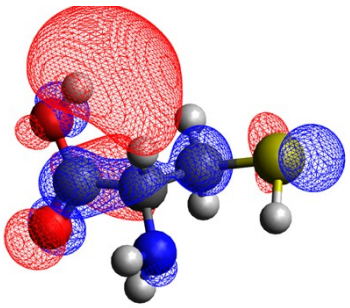
30 (HOMO–2)
E = –8.266 eV



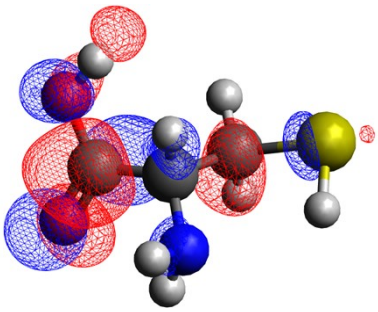
31 (HOMO–1)
E = –7.511 eV



32 (HOMO)
E = –6.728 eV

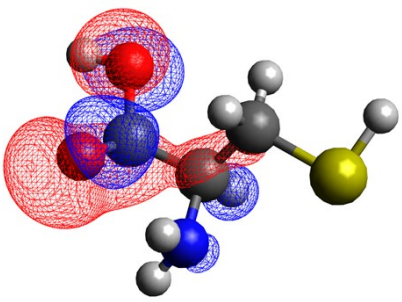


33 (LUMO)
E = –0.901 eV

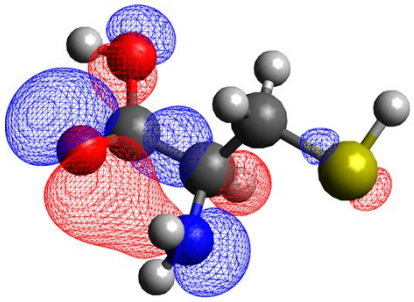


34 (LUMO+1)
E = –0.692 eV

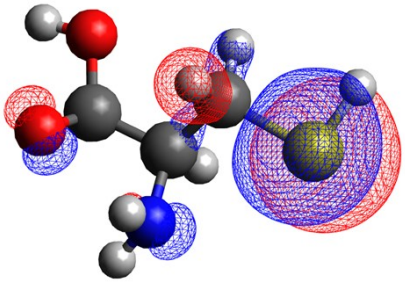
Figure. S5. Molecular orbitals of cysteine at the ground S_0 state geometry



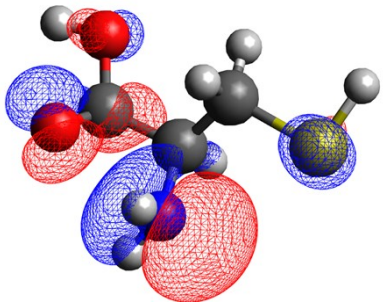
29 (HOMO–3)
E = –8.694 eV



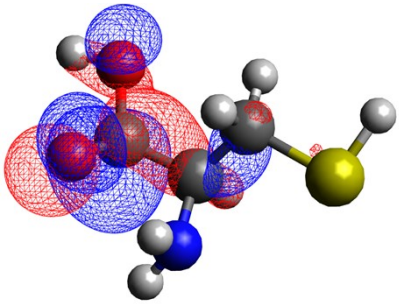
30 (HOMO–2)
E = –7.864 eV



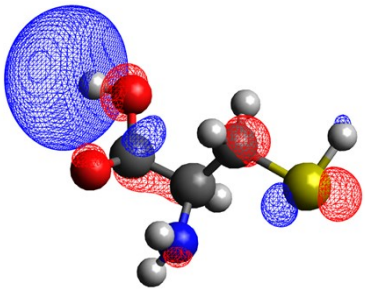
31 (HOMO–1)
E = –6.675 eV



32 (HOMO)
E = –6.415 eV

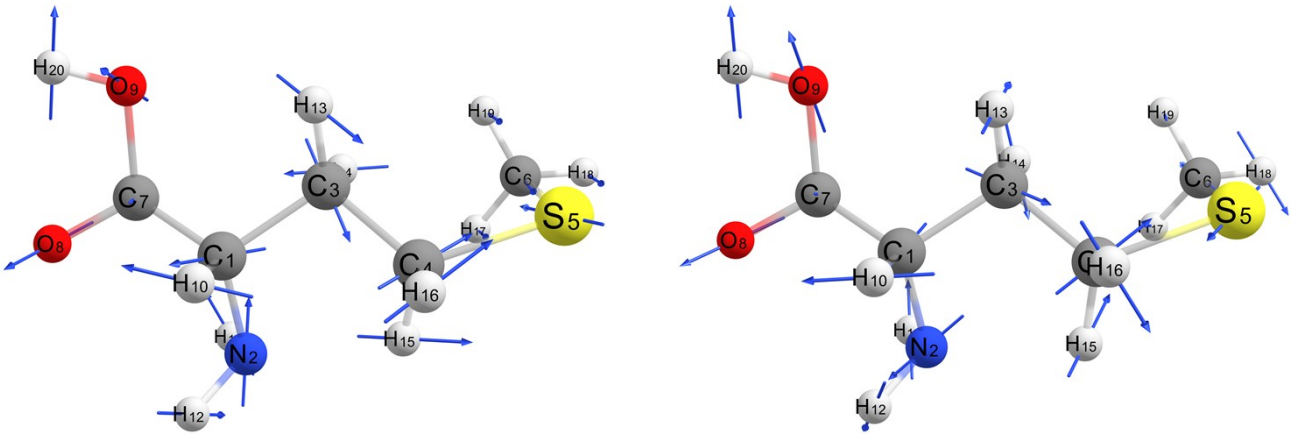


33 (LUMO)
E = –2.914 eV

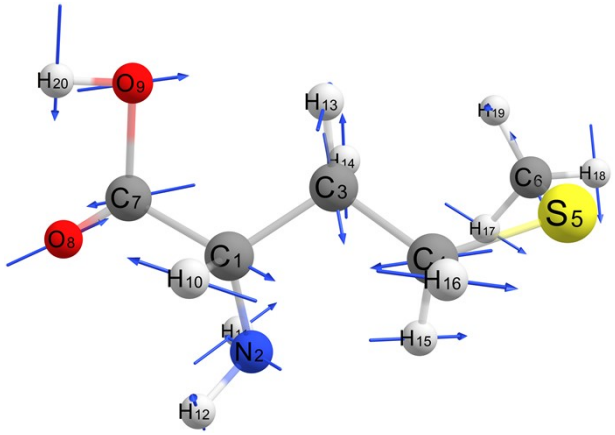


34 (LUMO+1)
E = –0.571 eV

Figure. S6. Molecular orbitals of cysteine at the ground T_1 state geometry obtained by TD-TDF method

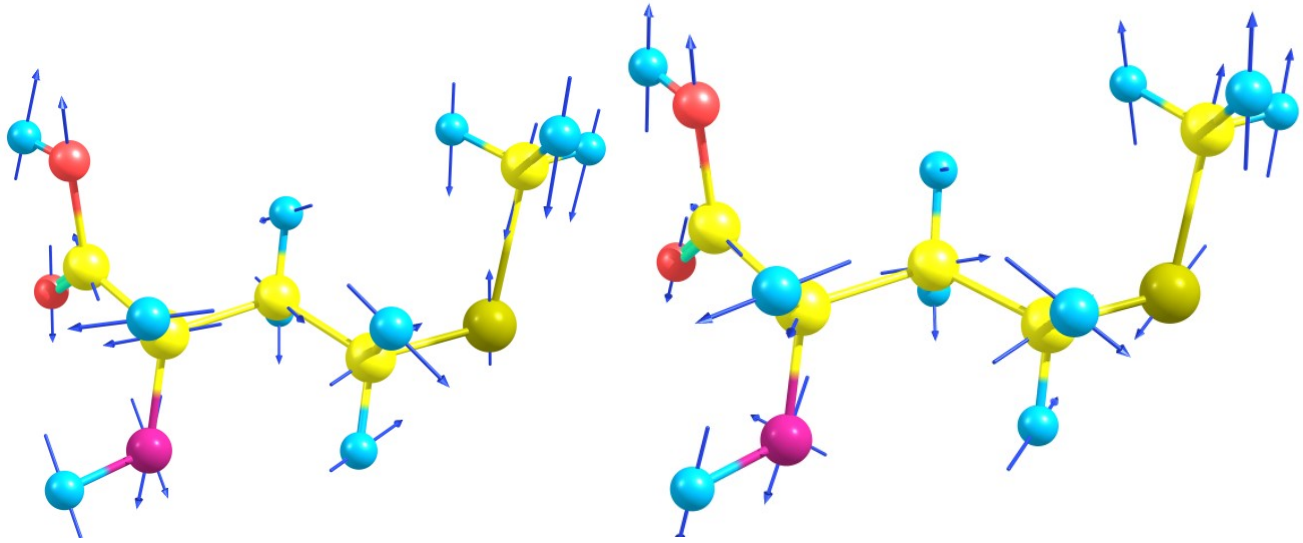


$\nu_{23} = 688.9\ cm^{-1}$ $\nu_{24} = 731.6\ cm^{-1}$



$\nu_{48} = 1511.58\ cm^{-1}$

Figure. S7. Vibrational modes in the optimized triplet T_1 state of L-methionine.



$\nu_{21} = 686.8\ cm^{-1}$ $\nu_{22} = 735.5\ cm^{-1}$

Figure S8. Vibrational modes in the optimized singlet S_0 state of L-methionine connected with symmetric and asymmetric C-S-C stretching vibrations.

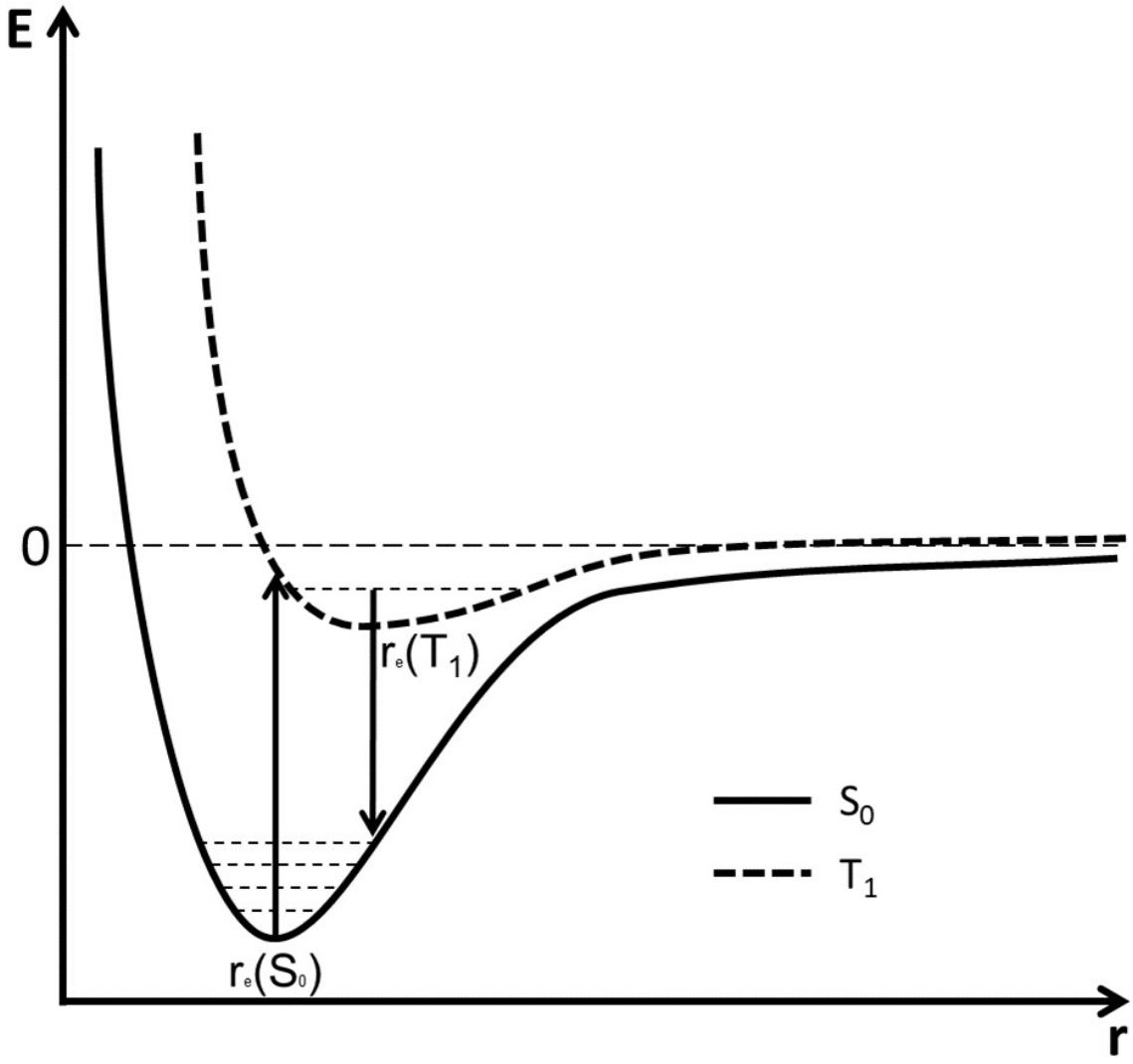


Figure S9. Typical potential energy curves for the singlet S_0 and triplet T_1 states

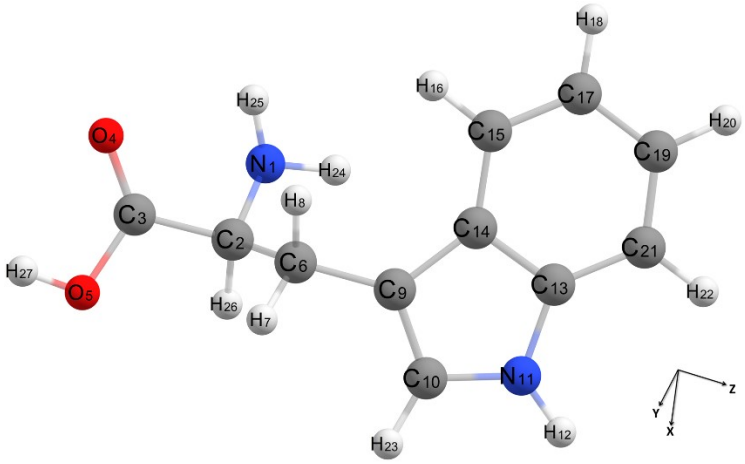
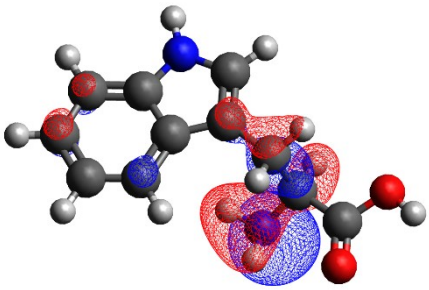
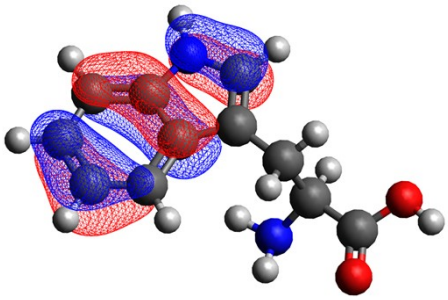


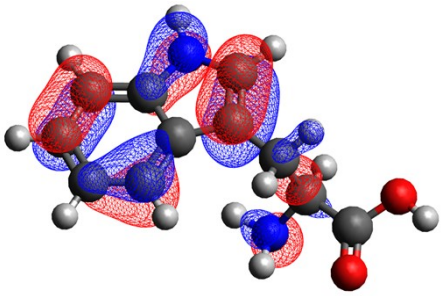
Figure. S10. Optimized structure of the Tryptophane ground state



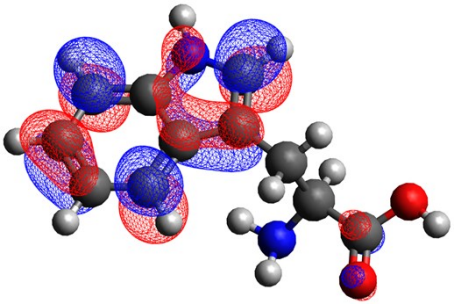
52 (HOMO–2)
E = –6.712eV



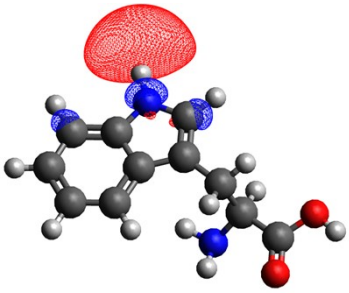
53 (HOMO–1)
E = –6.363 eV



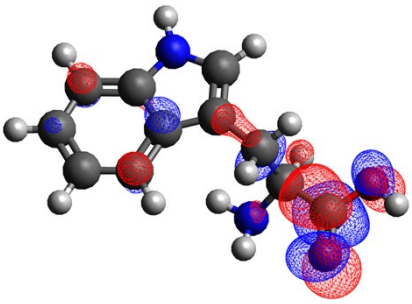
54 (HOMO)
E = –5.772eV



55 (LUMO)
E = –0.804 eV



56 (LUMO+1)
E = –0.406 eV



57 (LUMO+2)
E = –0.266 eV

Figure. S11. Molecular orbitals of tryptophan at the ground S_0 state geometry.